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Exposure and Risk Assessment for Silver

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This report assesses the risk of exposure to silver. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in June of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of silver in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to silver for various subpopulations.

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EPA-440/4-81-017
June 1981

AN EXPOSURE AND RISK ASSESSMENT
FOR SILVER

by

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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

Michael W. Slimak, Chief
Exposure Assessment Section
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Office of Water Regulations and Standards

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Gregory Kew, MDSD, was the project manager at the U.S. EPA.

CHAPTER I.

TECHNICAL SUMMARY

GENERAL STATEMENT OF RISK

Due to the low ambient concentrations of silver to which humans are exposed and the high concentrations required to elicit adverse effects, the likelihood of nonoccupational exposure to humans to harmful levels is low. In addition, metabolic factors such as the low efficiency of absorption through skin, lungs and gastro-intestinal tract, reduce the probability of adverse exposure.

The most likely adverse effect to occur from environmental exposure of humans is argyria, a localized non-lethal skin discoloration. However, the chronic accumulative exposure required to elicit the effect is unlikely to occur from ingestion and/or inhalation of typical environmental concentrations of silver.

Animal data indicate that chronic exposure to higher concentrations of silver may result in kidney hemorrhaging, this may not be applicable to humans. Based on extrapolation of results from one experiment on laboratory rats, the subpopulations likely to be exposed to concentrations high enough to elicit this effect are users of silver-containing medicinal products and people living in the vicinity of a government mint. The sizes of these subpopulations are expected to be very small. The subpopulation of amateur photographers who develop film in home darkrooms is not expected to be adversely exposed to silver based on a low dermal absorption efficiency and localization of any accumulated silver in the area of skin exposed.

There is some potential for environmental exposure of fish and aquatic invertebrates to harmful levels of silver in surface water. However, the actual likelihood of adverse effects is difficult to determine due to several factors. While silver in ionic form is one of the most toxic of the metals to fish and many aquatic organisms, fish and other aquatic organisms are physiologically more sensitive to silver than mammals due to a higher absorption efficiency through gill uptake and due to exposure to higher concentrations in water. Although surface water concentrations (as total Ag) are often reported at levels comparable to concentrations found toxic to biota (as measured in bioassays), only a fraction of the total silver concentration reported is biologically available. Therefore, the actual "effective" concentration may be significantly lower. Determination of this fraction requires knowledge of pH, concentration of complexing agents, water hardness and other variables. Without this knowledge and the requisite focus on a localized level, the conservative assumption must be made that a potential for adverse exposure of sensitive aquatic organisms exists and the likelihood of harm increases with conditions conducive to ionization of available silver.

Microbial populations, both in natural systems and wastewater treatment plants, do not appear to be sensitive to silver at typical environmental concentrations. Certain highly specialized locations such as in the immediate vicinity of cloud-seeding machinery or an activated sludge treatment plant which receives unusually high concentrations of silver may experience reductions in microbial activity. Due to the immobility of silver in soil and its propensity for adsorption onto sludge, any localized adverse effects would probably be long-term unless a silver resistant microbial population adapted to replace the more sensitive one.

HUMAN EXPOSURE AND EFFECTS

Human exposure to silver can occur through ingestion, dermal absorption or inhalation, but all three routes prove to result in low exposures. Figure I illustrates the potential exposure pathways to silver for humans as well as for fish and wildlife populations and shows their relationship to silver in various environmental media. The figure does not quantify the levels of exposure associated with each pathway.

Humans ingest silver in their diet and drinking water. Typical daily dietary exposure ranges from 35-88 ug, although higher levels are likely for certain subpopulations ingesting large quantities of silver-contaminated bran, mushrooms, fish or shellfish. The maximum daily exposure resulting from ingestion of drinking water is 0.06 mg, but the average is much lower. A small fraction of the U.S. population who customarily drink untreated surface water may be exposed to levels of silver exceeding EPA's Water Quality Criterion for protection of human health.

Dermal absorption is a significant exposure route only for patients suffering from major burns. In these cases, as much as 100 mg of silver may be involved per application although not all of this amount would be absorbed. Home processing of photographic film does not appear to be associated with a high level of silver uptake.

Inhalation of silver will expose large subpopulations in urban areas to exposure levels of approximately 45 ng to 185 ng per day. Very small subpopulations may be exposed to significantly higher exposure levels in the vicinity of smelters (approximately 450 ng/day but as high as 1576 ng), steel mills (up to 216 ng/day) and government mints (0.86 mg/day as a worst case, more likely 0.29 mg/day).

In conclusion, the highest human exposure levels are due to localized atmospheric concentrations of silver affecting small subpopulations and to medicinal use of silver-containing products. Exposure levels from ingesting untreated surface water may exceed the EPA drinking water standard; however, typical concentrations in drinking water are usually lower than the standard.

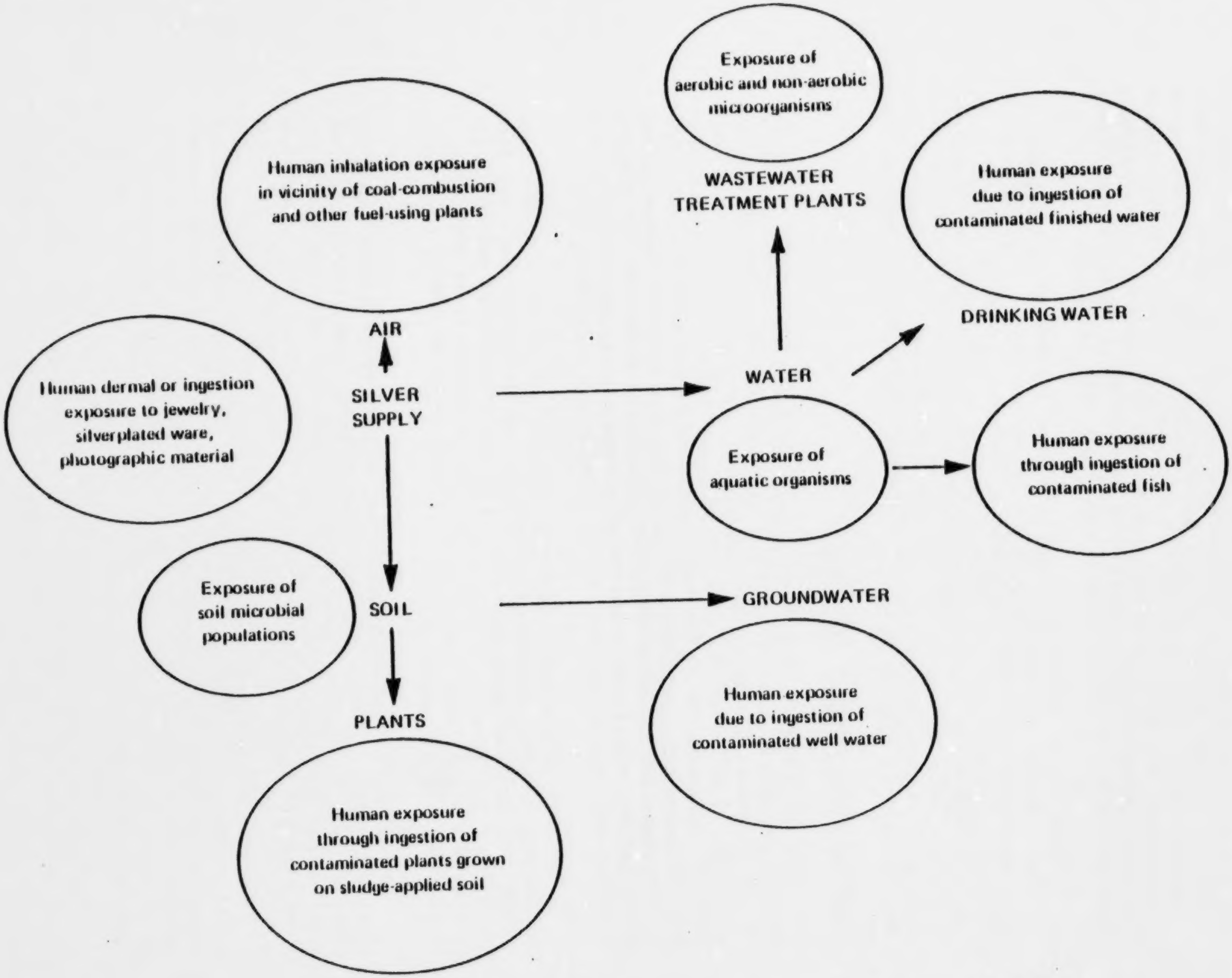
Human inhalation exposure in vicinity of coal-combustion and other fuel-using plants
AIR
Human dermal or ingestion exposure to jewelry, silverplated ware, photographic material
SILVER SUPPLY
Exposure of soil microbial populations
SOIL
PLANTS
Human exposure through ingestion of contaminated plants grown on sludge-applied soil
Exposure of aerobic and non-aerobic microorganisms
WASTEWATER TREATMENT PLANTS
Human exposure due to ingestion of contaminated finished water
DRINKING WATER
WATER
Exposure of aquatic organisms
Human exposure through ingestion of contaminated fish
GROUNDWATER
Human exposure due to ingestion of contaminated well water

FIGURE I POTENTIAL EXPOSURE ROUTES TO SILVER AFFECTING HUMAN AND NON-HUMAN BIOTA

Few data are available for adverse effects resulting from exposure to silver at different concentrations and exposure routes. Systemic toxicity is rare due to the poor absorption of silver by all routes of exposure (e.g., less than 10% by the oral route). The only known consequence of human exposure to silver is argyria. Considered a cosmetic defect with no significant physiological effects, argyria is believed to occur after retention of 1g or more of silver.

There is no evidence suggesting that silver is carcinogenic to humans. Silver has not been found to be carcinogenic to laboratory animals exposed through subcutaneous implantation of silver foil or colloidal suspensions. No chronic feeding or inhalation studies have been conducted on laboratory animals. The data now available on mutagenic effects appear to conflict so further investigation is required. Little information is available regarding the reproductive and teratogenic effects of silver.

NONHUMAN BIOTA EXPOSURE AND EFFECTS

The environmental medium of primary interest for fish and wildlife exposure is water. Soil is of more direct interest to human exposure due to the potential for bioaccumulation in edible plants grown in silver-contaminated soil. Air does not appear to provide a significant exposure route to nonhumans due to the small amount of silver released to air from any source and the short half-life of silver in air. Small subpopulations in the immediate vicinity of sources (smelters, mints) may be affected but it was not possible to quantify this route due to lack of appropriate toxicity information and lack of source-specific monitoring data.

The most significant cultural sources of silver to water are discharges from the photographic industry (totaling 109 kkg) and from mining, milling, smelting and refining of silver and other metallic ores (totaling 5 kkg annually). Publicly Owned Treatment Works (POTWs) also discharge a significant amount of silver to water following treatment, an estimated 70 kkg annually.

Typical fresh surface water concentrations range from 0.1 ug/l to 10 ug/l of total silver. Higher concentrations, however, are observed with 10% of all positive observations between 10.1 ug/l and 100 ug/l. Observations reported in marine water are fewer and tend to be lower than those reported in freshwater.

As stated previously, silver is toxic at low concentrations to aquatic life. Acute effects levels vary by species and experimental procedure but generally range from 4.3 ug/l to 100 ug/l for freshwater fish and 1.5 to greater than 1000 ug/l for freshwater invertebrates. A "no effects" level between 0.09 and 0.17 ug/l was established for chronic exposure of rainbow trout.

Toxicity of silver has been attributed to the metal's induction of mucous secretion in the gills leading to suffocation. Other hypotheses suggested are blocking of essential enzymes and destruction of gill epithelial tissue.

Environmental parameters influencing aquatic toxicity of silver include: 1) water hardness--toxicity decreases with increasing hardness, and 2) size of fish--smaller animals are more susceptible. Other variables determining toxic levels of metals as a group such as pH, presence of complexing agents, salinity, etc., will also affect silver availability and toxicity.

MATERIALS BALANCE

Releases Due to Human Activities: Approximately 4640 metric tons of silver were used in the United States in 1978. Over 40% of this total was used in the manufacture of photographic materials. Manufacture of electrical and electronic components consumed an additional 25% of the total. These and other uses are illustrated in Table 1 on page 16.

While domestic ores are a significant source of silver (1225 kkg/yr), approximately twice as much (2354 kkg) is imported in a variety of forms. Recycling of silver (from a variety of sources) is widely practiced, accounting for 1150 kkg of U.S. refined silver production in 1978.

Consumer use and disposal of products containing silver eventually releases more silver to the environment than ore mining, processing, smelting and subsequent reprocessing combined. A large proportion (77%) of the silver discharged goes to landfills and approximately 10% goes directly to surface water. Around 7% goes to POTWs, and 6% to air. Further details may be found in Table 2, page 18.

The most significant manmade sources of silver air emissions are the silver smelting and refining industry (30%), municipal waste incineration (13%) and inadvertant sources such as from fossil fuel combustion, cement manufacture and iron and steel production/manufacturing (23% total).

Photographic manufacture and processing are the only manmade sources of silver going to POTWs or discharged directly to surface waters (although POTW pass-through of silver accounts for a tonnage equal to 33% of the total going to surface waters due to human activity).

The largest contributions to the landfilled or land-applied silver burden are from photographic manufacturers and processors (62%), silver mining, processing, and refining (16%), and from POTW sludge whose contribution is equivalent to 22% of all manmade sources.

Natural Releases: Natural releases of silver to the U.S. environment are mostly attributable to the weathering of minerals. These mechanisms result in release of around 440 kkg/yr to freshwater streams and rivers and deposition of approximately 40 kkg of silver in sediments, largely in the form of very insoluble oxides and sulfides.

Very small quantities of silver also are released to the U.S. environment as dust carried in sea salt spray, but these are negligible in comparison to the quantity due to weathering of minerals which is released to the water and sediment. The global burden of silver in the atmosphere due to all types of dust has been estimated as 50 kkg/yr. Sea salt spray contributes only around 2 kkg/yr to the global burden.

ENVIRONMENTAL PATHWAYS OF SILVER

Figure II roughly illustrates the flow of silver throughout the different environmental media based on materials balance and fate pathway information. Interaction between environmental compartments is low due to the immobility of silver in most soils, its tendency to associate tightly with sediment in aquatic systems, and its very low release rates to the potentially more dynamic air compartment.

The fate and distribution of silver following release to the environment can be characterized by one of four source-dependent pathways: atmospheric emissions (accounting for 6% of total manmade releases), land disposal of solid waste including mine tailings (77%), aquatic discharges to surface water (10%) and aquatic discharges to POTWs (7%).

Atmosphere: Atmospheric emissions originate from smelting activities, inadvertent releases (fuel combustion, steel manufacturing, etc.), and certain silver-consuming industries. Particles of less than 20 um diameter (from smelting and combustion) will be widely dispersed in the atmosphere in the form of oxides, sulphides, sulphates and chlorides, eventually reaching land and water via rainout and dry deposition. Particulates larger than 20 um in diameter (from smelters) are likely to settle out within 1 km of the source of emission. The form of silver in these particulates is expected to be the same as in the ore undergoing smelting.

Levels of silver present in air in both urban and rural regions generally are less than 5 ng/m^3. Levels in the vicinity of some inadvertant sources such as coal-fired steam plants or steel mills are not notably higher. However, levels in the vicinity of some metal smelters may be depending on the silver concentration in the ore. For example, levels of up to 36.5 ng/m were detected near a lead smelter processing ores known to contain high silver concentrations. Cloud seeding activities only result in increased air levels in the immediate vicinity of the land-based equipment used.

Land: The largest contributions to the landfilled or land-applied silver burden are from photographic manufacturers and processors (62%), silver mining, processing, and refining (16%), discard of electrical equipment having silver contacts and conductors (15%), and from POTW sludge whose contribution is equivalent to 22% of all manmade sources.

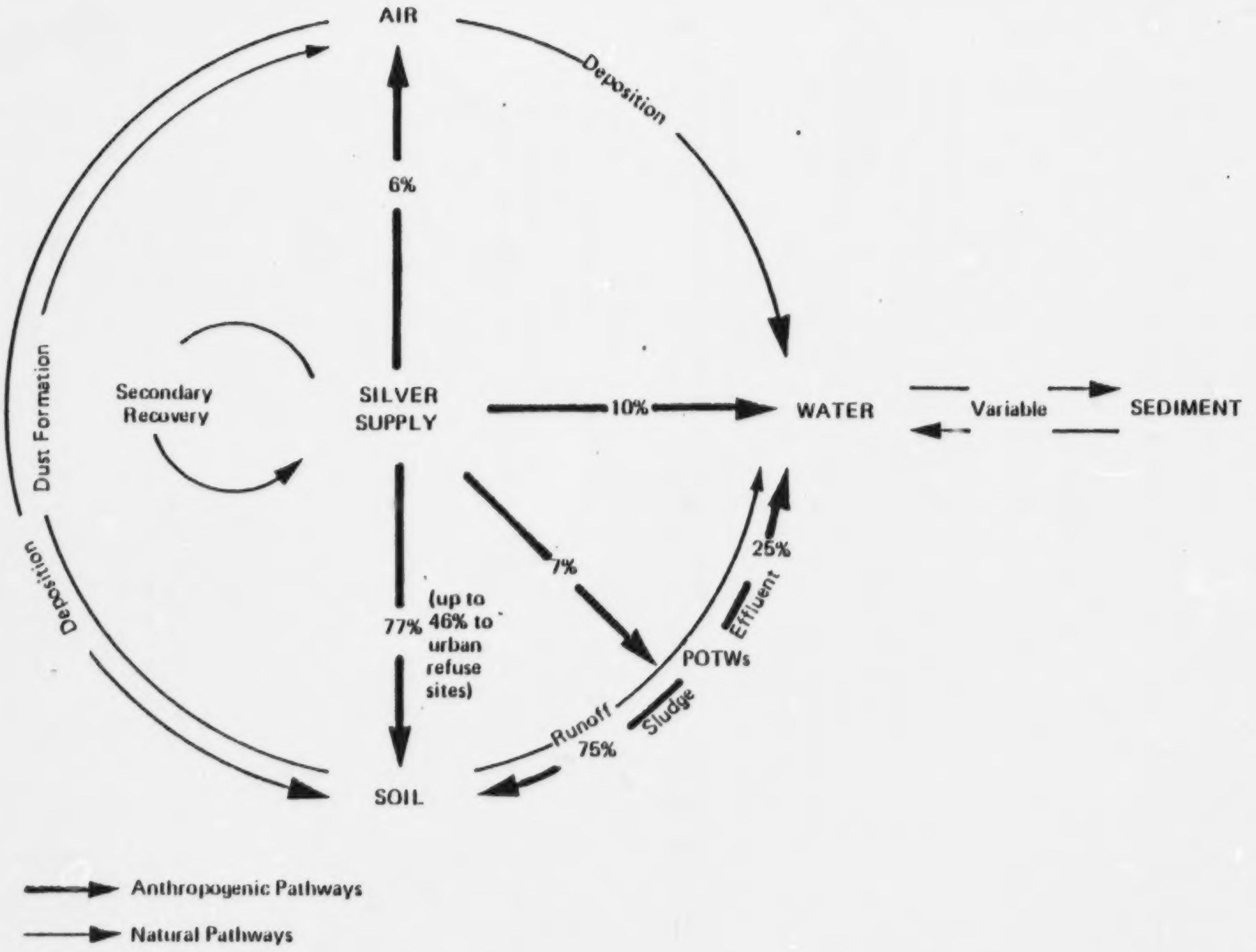
AIR
Deposition
6%
Dust Formation
Secondary Recovery
SILVER SUPPLY
10%
WATER
Variable
SEDIMENT
7%
25%
Effluent
POTWs
Sludge
Runoff
75%
77%
(up to 46% to urban refuse sites)
Deposition
SOIL
Anthropogenic Pathways
Natural Pathways

FIGURE II ANTHROPOGENIC FLOW OF SILVER THROUGH THE ENVIRONMENT

Acid mine drainage does not appear to be an important contributor of silver releases. Once in the soil, the element is relatively immobile, with little potential for leaching into groundwater. Because silver accumulates in the upper soil layer following soil surface application or disposal, it may be transported to water through runoff.

Silver concentrations in soil are more commonly derived from parent rock rather than cultural sources. Typical ambient levels reflect the substrate concentration and thus are variable, ranging from 0.02 mg/kg to as high as 1000 mg/kg. An average natural background level is approximately 0.1 mg/kg to 0.2 mg/kg. Silver in sludge or other wastes being disposed of on land is at concentrations as high as 900 mg/kg, although 100 mg/kg is more typical. No information was available on levels at landfill sites following incorporation of the waste.

Background concentrations of silver in terrestrial plants ranged from 0.02 mg/kg in alfalfa tops to 5.5 mg/kg in mushroom caps. Experimental data indicate that silver may be accumulated from solution at concentrations as high as 1760 mg/kg in bush beans. In most cases, however, accumulation is not so extreme. Specific food crops with reported silver residues included whole wheat (0.4 mg/kg), wheat germ (0.8 mg/kg), tea (2 mg/kg), and fruits and nuts (up to 1 mg/kg).

Although data on accumulation of silver in terrestrial organisms are limited, silver does not appear to have a strong potential for biomagnification in terrestrial food chains.

Water: Effluents containing silver are discharged by the photographic industry, both in production and development, by electroplaters and by smelters. Most companies practice in-house recovery techniques using precipitation, ion exchange, electrolytic recovery, and/or reductive exchange. Fifty percent of the photographic producers discharge to POTWs. Amateur photographers discharge untreated wastes, primarily to POTWs, however, the total amount is small. In surface water, the fate of the silver is dependent on the form discharges. Thiosulfate silver complexes, which are the primary form released by the photographic industry, are degraded slowly and then precipitated as a halide or sulfide. The distribution of silver ions between the freeform and complexes is dependent upon pH, redox potential, and the presence of complexing agents. According to the results of a chemical speciation model, $AgCl_2$ is the most prominent form in maring waters, with only negligible amounts of the ionic form; in freshwater in the presence of sulfur, AgHS predominates, especially in areas of low salt concentrations. In freshwater streams, approximately 10% of the total load of silver is found in suspended sediment. Silver accumulates in bottom sediments in the vicinity of sources, especially in the surface layer.

Monitoring data for total silver levels in U.S. surface water indicate typical annual mean concentrations of less than 10 ug/l. Regions with higher than average concentrations include the North Atlantic, South Atlantic, and North Mississippi River basins. Samples from groundwater in mining areas revealed concentrations even lower than the national average.

Sediment levels of silver in surface water usually range from 1 mg/kg to 10 mg/kg, with a high a 95 mg/kg; sediment concentrations are usually two to three orders of magnitude above water levels. In dissolved and suspended matter in rivers, silver concentrations ranged usually from 0.1 ug/l to 7 ug/l in 1968. More recent data indicate that levels were usually less than 0.06 mg/l. Levels to surface waters in effluent industrial wastewater, and sewage treatment discharges are generally less than 20 ug/l (mean values), with a maximum of 730 ug/l.

The mean concentration of silver in fish from U.S. river basins according to STORET is 0.235 mg/kg, with a range of 0.004 to 1.9 mg/lg. Other studies report levels up to 9 mg/kg (in shellfish) and 4.4 mg/kg in bone tissue of cut-throat trout. In general, however, most concentrations rarely exceed 1.0 mg/kg in marine and freshwater fish and invertebrates. Reported bioconcentration factors (tissue levels/water levels) range from 2.4 to 333 for various freshwater fish species. Marine species, according to the available data, have a greater tendency to accumulate silver up to levels that are 3300 times the concentration in surrounding seawater. Both marine and freshwater plants are reported to concentrate silver by a factor of 200; typical measured concentrations are less than 1.0 mg/kg.

POTWs: Wastewater treatment techniques such as lime and settling, activated carbon, and cation-exchange are over 90% effective in removing silver from influents. However, these techniques are not used in most POTWs. In facilities utilizing more conventional technology, 75% of the silver is partitioned into the sludge leading to concentrations of 100 mg/kg or greater.

CHAPTER II.

INTRODUCTION

The Office of Water Planning and Standards, Monitoring and Data Support Division, of the U.S. Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and estimate the risk of receptor exposure to these substances. The results are intended to serve as a basis for evaluating the magnitude of the risk and developing suitable regulatory strategy for reducing any such risk when action is warranted.

This report provides a brief, but comprehensive, summary of the manufacture, use, distribution, fate, effects and potential risk of silver ot humans and nonhumans. Making effective use of the information given requires an understanding of uncertainties regarding the data and qualifications regarding conclusions presented herein.

Silver is found naturally at low levels in the earth's crust and various environmental media. The amount released annually from these sources to air and water is an important factor in the assessment of the environmental impacts due to human activity. However, natural loading rates are difficult to estimate and are not known with great certainty.

As is characteristic of inorganics in general, silver is commonly found in association with other metals. Although silver is relatively toxic to aquatic life, its concentration is usually significantly lower than those of other metals, thus reducing its contribution to the overall effect of the mixture. In some cases, synergistic effects may result from associations with different metals.

Silver's market value encourages intensive recovery practices for industries which produce and consume the metal. Wherever possible, knowledge on current recovery practices for specific industries were used to try to make realistic estimates of their emissions. Estimates of silver loading from industrial sources are based on treated effluent concentrations whenever possible. Otherwise, raw wastewater concentrations are used which may result in an overestimate of that particular release.

The report is organized as follows:

> Chapter III presents a materials balance for silver that considers quantities of the chemical consumed in various applications, the form and amount of pollutant released to the environment, the environmental compartment initially receiving it, and, to the degree possible, the locations and timing of releases.
>
> Chapter IV describes the distribution of silver in the environment by considering the critical environmental pathways for silver that determine its fate in the environment and describing the distribution of the element in the environment reported in monitoring data.
>
> Chapter V considers toxicological effects and exposure to non-human biota, predominantly aquatic biota and microorganisms.
>
> Chapter VI describes the available data concerning the toxicity of silver for humans and laboratory animals and quantifies the likely level of human exposure via major known pathways.
>
> Chapter VII presents likely exposure conditions for nonhuman biota and presents various exposure scenarios for humans; the exposure levels are correlated with reported effects levels from Chapters V and VI, in order to assess the risk presented by environmental exposures to silver.

CHAPTER III.

MATERIALS BALANCE

A. INTRODUCTION AND METHODOLOGY

An environmental materials balance for silver presented in this chapter considers man-made releases of the metal to the first point of entry into the environment. Natural releases are also briefly considered. Potential sources of silver releases were identified by a review of industrial activities involving the metal, including extraction, refining, use, and disposal. The amount of silver used by man was followed as best as possible from the original sources through its life cycle of production and uses to final disposal. At each stage in the life cycle, potential releases to the environment were identified.

For each source of pollutant release, the amount of material emitted, the process point at which the emission occurred, and the environmental compartments (water, air, and soil) initially receiving and transporting the metal were identified. In addition, the locations for sources of releases were distinguished when sufficient information was available. There are many uncertainties inherent in this type of analysis: not all current releases have been identified and past and future patterns of production, use, and disposal are difficult to determine. However, sufficient information is available to provide a general picture of the anthropogenic environmental loading of silver in terms of nature, magnitude, and location.

The scope of the materials balance has been limited to a review of published and unpublished data concerning sources of silver releases to the environment. The available literature has been critically reviewed and compiled in order to present an overview of major sources of silver emissions, annotated tables containing assumptions and estimations used in deriving numbers, and an indication of data gaps. Data collection was significantly aided by Smith and Carson's (1977) comprehensive review concerning silver in the environment.

B. OVERVIEW

The 1978 U.S. industrial demand for silver was approximately 4640 kkg; an additional 700 kkg was exported in unprocessed form and silver-containing products. The sources of silver in the U.S. are both domestic and foreign. Table 1 summarizes the industrial supply of and demand for silver in 1978.

Silver occurs commonly and is widely distributed at low concentrations in crustal deposits; therefore water, soil, and air contain low background levels of the element. Silver is produced

TABLE 1. SUMMARY OF U.S. SILVER SUPPLY AND DEMAND, 1978

Source/Consumer	Supply (kkg)	Consumption (kkg)
U.S. Mine Production	(1,230)[1]	
Primary Smelting and Refining (of ores)	1,690	
Secondary Smelting and Refining (of (of scrap)	1,150	
Imports (ore, dore, scrap)	450	
Imports (refined metal)	1,910	
U.S. Stocks	5,990	
Photographic Material		2,000
Contacts/Conductors		960
Sterling Ware		560
Brazing Alloys/Solders		340
Other		920
Exports		700
U.S. Stocks		5,850
	11,190	11,190

[1] This number is not included in the total in order to prevent double-counting of amounts for primary smelting.

Note: The above figures are estimations for the year 1978. Due to considerable yearly statistical variation, these values do not necessarily represent typical annual levels of production and use.

from mining and milling of various ores containing the metal at concentrations from 1 mg/kg to almost 1000 mg/kg. Additionally, since a large amount of silver is contained in discarded products, the recycling of this scrap is also an important source of silver. Unintentional production of silver occurs both through cultural activities and natural processes.

Environmental releases of silver during production processes and consumptive uses are presented in Table 2 and Figure 1 and 2 The largest single discharger of silver to water and soil is the photographic industry during manufacture of products and film development. This is not surprising since the photographic industry consumes 43% (including the products exported) of the annual U.S. total consumption of silver. Other major releases are generated by milling activities, primary smelting, and from production, use, and disposal of contact/conductors and brazing alloys/solders, which are significant silver consumers. Less important releases come from secondary smelting and inadvertent sources such as cement manufacturing, fuel combustion, and iron and steel production.

A special category of releases to the environment are those from Publicly Owned Treatment Works (POTWs) and urban refuse landfills. Some portion of the releases to water and land are made directly to POTWs and landfills for subsequent release to various environmental media. These releases are shown separately from those of other anthropogenic sources in order to avoid possible double counting.

C. METALS PRODUCTION

1. Mine Production

Underground and open-pit mining of silver, copper, lead, gold, and zinc ores produced 1225 kkg of recoverable silver in 1978 (Drake and Butterman 1979). Underground mining involves drilling and blasting tunnels and shafts and raising the ore to the surface for transport. Open-pit mining requires the removal of overburden, thereby exposing the ore to the surface, where it is drilled, blasted and transported for further processing. Table 3 lists 1978 mine production of recoverable silver by state. Major silver-producing mines (accounting for about 50% of annual production), ore type, and location are shown in Table 4.

Silver ores are the most important source of silver, accounting for nearly one-half of total mine production. Much of this ore is found in the Coeur d'Alene district of Idaho, which is one of the major silver-lead-zinc producing areas in the world. In 1978, the Sunshine Mine, located in this area, produced 154 kkg of silver from ore with a silver concentration of approximately 860 mg/kg (Lindstrom 1979).

TABLE 2. SUMMARY OF ESTIMATED ENVIRONMENTAL RELEASES OF SILVER, 1978

	Release (kkg/year)			
Source	Direct Aquatic	POTW	Air	Land
Metals Production				
Mining and Milling	1	-	3	62
Smelting and Refining (primary)	2	-	19	103
Smelting and Refining (secondary)	2	-	8	-
Other Production in Which Silver is a Byproduct				
Cement Manufacture	-	-	2	2
Coal and Petroleum Combustion	-	-	9	-
Iron and Steel Production	-	-	7	-
End Uses				
Photographic Industry				
• manufacture	54	88	4	630
• developing	65	-		
Contact/Conductors	-	-	22	150
Sterling Ware	-	-	1	
Brazing alloys/Solders	-	-	2	60
Catalysts	-	-	0.01	-
Electroplated Ware	1	-	-	-
Jewelry	-	-	0.4	-
Batteries	0.03	-	-	-
Commemorative Coins, Medallions	-	-	-	-
Dental/Medical	0.003	-	-	-
Mirrors	-	-	0.05	-
Bearings	0.06	-	-	-
Cloud Seeding	-	-	-	2[1]
Coinage	-	-	-	-
Total from anthropogenic sources	125	88	77.7	1009 = 1300
	(10%)	(7%)	(6%)	(77%)= (100%)
POTWs	70		-	220
Urban Refuse[4]	-		10	370-520
Natural Emissions	438	-	___[2]	NE[3]
Urban Runoff	72	96	-	-

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[1] Actually discharged to both surface water and land.

[2] Global estimate of 52 kkg per year. (See Table 19.)

[3] Not estimated

[4] Includes land disposal of products listed above.

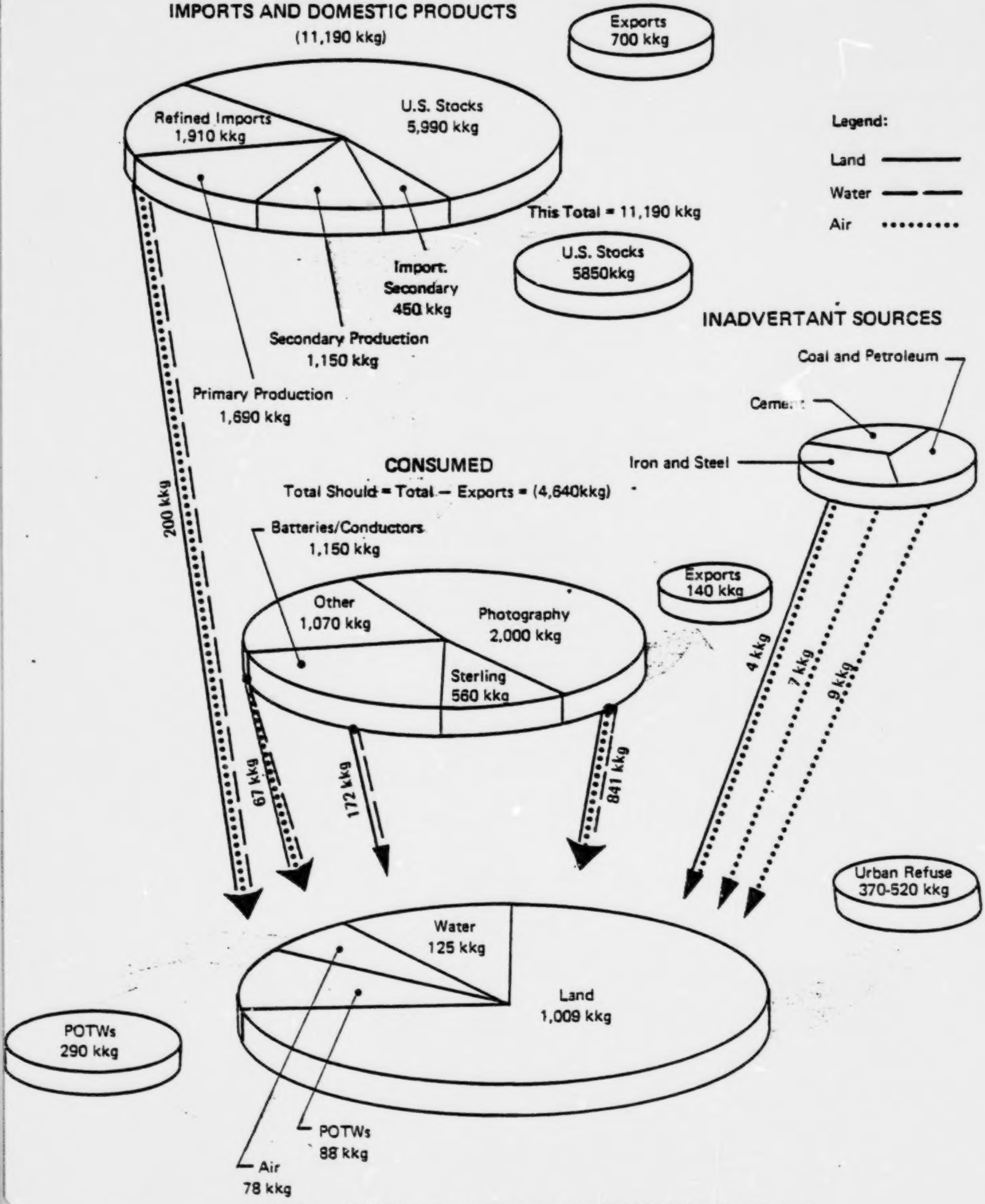
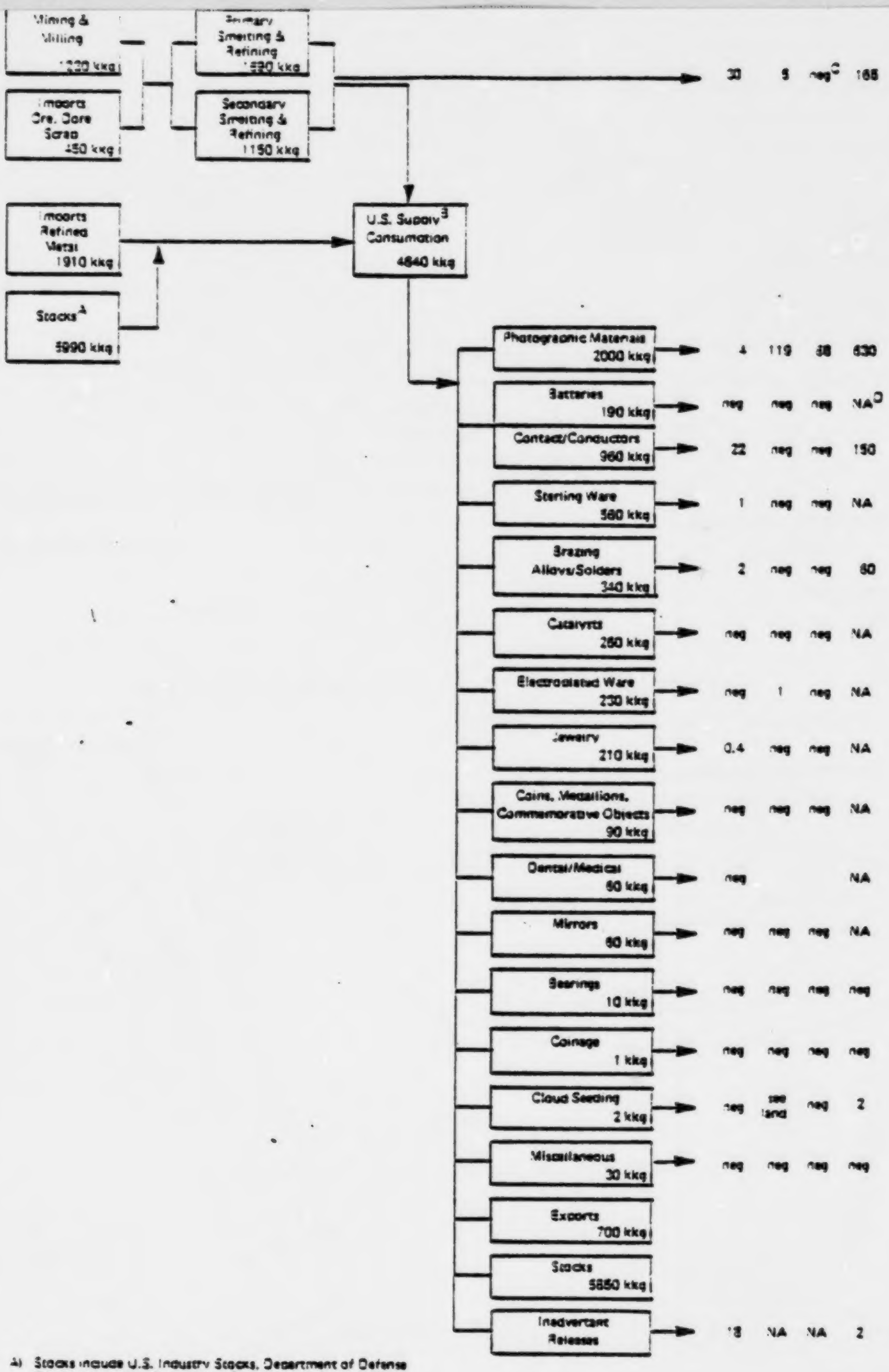

IMPORTS AND DOMESTIC PRODUCTS
(11,190 kkg)
Exports
700 kkg
Refined Imports
1,910 kkg
U.S. Stocks
5,990 kkg
Legend:
Land
Water
Air
This Total = 11,190 kkg
U.S. Stocks
5850kkg
Import
Secondary
450 kkg
Secondary Production
1,150 kkg
Primary Production
1,690 kkg
INADVERTANT SOURCES
Coal and Petroleum
Cement
Iron and Steel
CONSUMED
Total Should = Total – Exports = (4,640kkg)
200 kkg
Batteries/Conductors
1,150 kkg
Exports
140 kkg
Other
1,070 kkg
Photography
2,000 kkg
Sterling
560 kkg
4 kkg
7 kkg
9 kkg
67 kkg
172 kkg
841 kkg
Urban Refuse
370-520 kkg
Water
125 kkg
Land
1,009 kkg
POTWs
290 kkg
POTWs
88 kkg
Air
78 kkg

FIGURE 1 MATERIALS BALANCE OF ANTHROPOGENIC SILVER, 1978


Mining & Milling
1220 kkg
Primary Smelting & Refining
1630 kkg
Imports Ore, Dore Scrap
450 kkg
Secondary Smelting & Refining
1150 kkg
30 5 neg[C] 165
Imports Refined Metal
1910 kkg
Stocks[A]
5990 kkg
U.S. Supply[B] Consumption
4840 kkg
Photographic Materials
2000 kkg
4 119 88 630
Batteries
190 kkg
neg neg neg NA[D]
Contact/Conductors
960 kkg
22 neg neg 150
Sterling Ware
580 kkg
1 neg neg NA
Brazing Alloys/Solders
340 kkg
2 neg neg 60
Catalysts
260 kkg
neg neg neg NA
Electroplated Ware
230 kkg
neg 1 neg NA
Jewelry
210 kkg
0.4 neg neg NA
Coins, Medallions, Commemorative Objects
90 kkg
neg neg neg NA
Dental/Medical
60 kkg
neg NA
Mirrors
60 kkg
neg neg neg NA
Bearings
10 kkg
neg neg neg neg
Coinage
1 kkg
neg neg neg neg
Cloud Seeding
2 kkg
neg see land neg 2
Miscellaneous
30 kkg
neg neg neg neg
Exports
700 kkg
Stocks
5850 kkg
Inadvertent Releases
18 NA NA 2

A) Stocks include U.S. Industry Stocks, Department of Defense Stocks, New York Commodity Exchange and Chicago Board of Trade Stocks, and Treasury bullion.

B) Supply does not include old scrap recycled at factory/refinery or accumulated stock from previous years in which supply exceeded demand.

C) Negligible

D) Not Available

Source: After Drake, 1978.

FIGURE 2 U.S. SILVER MATERIAL BALANCE: 1978

TABLE 3. MINE PRODUCTION OF RECOVERABLE SILVER BY STATE, 1978

State	Production (kkg)
Alaska	0.064
Arizona	206.4
California	1.80
Colorado	131.2
Idaho	571.6
Michigan	10.99
Missouri	63.9
Montana	90.8
Nevada	25.0
New Mexico	27.8
New York	0.650
Oregon	0.053
South Dakota	1.65
Utah	89.7
OTHER[1]	3.22
TOTAL	1224.8

---

[1] Includes Illinois, Tennessee, Texas, Washington.

Source: Drake and Butterman (1979).

TABLE 4. MINE PRODUCTION OF SILVER BY ORE TYPE AND MINE, 1978

Ore Type[1] and Mine	Location (State)	Method of Mining	Production (kkg)
Silver Ores			
Sunshine	Idaho	Underground	154
Galena	Idaho		124
Coeur	Idaho		75
Bulldog Mt.	Colorado		65
Crescent	Idaho		N/A
Sherman Tunnel	Colorado		N/A
DeLamar	Idaho	Open Pit	61
Copper Ores			
Berkley Pit	Montana	Open Pit	73
Mission	Arizona		15
Utah Copper	Utah Copper	Open Pit	N/A
Lead Ores			
Lucky Friday	Idaho	Underground	77
Gold Ores			
Homestake[2]	South Dakota	Unknown	2

---

[1] Ore types from Drake (1978).

[2] Jeffries and Tczap (1978).

Note: N/A = Not available

Source: Lindstrom (1979).

Copper ore, containing 1-3 mg/kg silver, accounted for 31.6% of the mine production of recoverable silver in 1978 (Drake 1979). Open-pit mining of copper ore is practiced more frequently than underground mining. Silver as a byproduct from copper ore in the U.S. comes mainly from Utah, Arizona, New Mexico, and the Keweenaw district of Michigan (Smith and Carson 1977).

Lead, gold, zinc, and complex copper-lead-zinc ores yield the remaining 13.2% of the total silver mined. Underground mining of silver-containing lead ore, mainly in Idaho and Michigan, provided 5.2% of the U.S. silver production in 1978 (Drake 1979). Silver produced from gold ore, recovered in South Dakota and Nevada by underground, open-pit, or placer methods, produced 17 kkg silver in 1978 (Drake 1979). Zinc and complex copper-lead-zinc ore provided 8% of the recoverable silver in 1978. Zinc ore bearing 34 mg/kg silver is found in Colorado and New York. Complex ores occur as veins in fracture zones and are mined chiefly in Idaho and Colorado, generally by underground mining techniques.

Losses of silver from mining of various ore types do not appear to be significant. Particulate emissions of silver are assumed to occur during drilling and blasting operations, but no specific data were found. Mine drainage from precipitation, groundwater, and runoff from water sprayed for dust control apparently discharge little silver to the environment. Smith and Carson (1977), for example, report silver concentrations ranging from 1 mg/l to 8 mg/l in drainage of abandoned mines. Larsen et al. (1973), in a study concerning treatment of metal-containing mine drainage, stated that "very little silver" was found in mine drainage of the Red Mountain mining district in Colorado, even though silver, lead, and gold were "extensively mined" in the area.

2. Milling of Silver-Containing Ores

Milling is the beneficiation of mined ore to yield a mineral concentrate. Silver-containing ores are milled most frequently by flotation processes based upon the hydrophobic or hydrophilic character of minerals such as silver sulfide. Other methods such as gravity concentration, and amalgamation-cyanidation are less common.

Flotation of all ore types involves crushing, grinding, and classification of the ore; the actual flotation processes and cleaning and conditioning of mill pulp are dependent upon the specific ore type and the metal content, but generally involve the following steps: A slurry of finely ground particles is agitated in a tank (flotation cell) and, as air is forced through the tank, air bubbles attach to non-wettable minerals. Frothing agents and conditioning agents are added to "float" or separate the minerals by species. Separation is effected by skimming the stabilized froth and withdrawing wettable mineral from the tank bottom.

Gravity concentration is used in milling of silver-bearing lead-zinc-ore in the Coeur d'Alene district in Idaho, the Tri-State district (Missouri, Kansas, and Oklahoma), and the Old Dick copper-zinc mill in Arizona (Smith and Carson 1977). The method used today is a fluid medium, in which minerals sink or float depending upon their densities relative to that of the medium (Smith and Carson 1977).

Amalgamation and cyanidation, involves grinding the ore to a coarse size, gravity separation of the metal containing black sands, and concentration of the metal by batch amalgamation of the sands (addition of mercury), to form an alloy (Schack and Clemmons 1963). Metal is recovered by grinding the amalgam to eliminate solid impurities; squeezing the amalgam through heavy canvas to remove excess mercury; retorting; and distilling to give a molten gold-silver bullion, which is transported to a smelter (Smith and Carson 1977). Amalgamation is used by the Homestake Mine in South Dakota and for recovery of placer gold from Alaska and western states.

In cyanidation, the ore is ground and classified into slime and sand fractions; precious metals from each fraction are first extracted with cyanide solution and subsequently precipitated using zinc shavings or dust. The precipitate is then melted, usually in a reverberatory type furnace to yield dore metal, a gold-silver concentrate (Schack and Clemmons 1963).

The total loss of silver to all environmental media during milling in 1978 is estimated to be 66 kkg (Table 5). Silver emissions to the air occur during crushing and grinding of the ore. The particles are relatively large and settle quickly (Smith and Carson 1977).

The wastewater from milling operations--flotation, cyanidation, and amalgamation--is sent to tailing ponds for settling, and in some cases a final clarification pond (U.S. EPA 1975c). Because floation process water is normally alkaline (pH 8), heavy metals, including silver, are precipitated in tailing ponds. Wastewater discharge from silver milling is further reduced by recycling of the settling pond decant. Negligible amounts of silver are reported to be discharged (U.S. EPA 1975c).

Tailing ponds are, however, responsible for relatively large discharges of silver to land. Mill residue consisting of process water and waste rock is pumped to these ponds, where the solids are settled and the water is either recycled to the mill or discharged directly. The amount of silver discharged from tailing ponds depends upon the specific milling practices and metal recovery processes for different ore types. Reports prior to 1977 indicate that 32% of the available silver in Missouri lead ore was lost to tailings during milling operations (Smith and Carson 1977). The total amount of silver lost in such ores is not extensive, however, because the silver concentration of the ore is low. Loss of silver to tailings during milling of silver ore in Idaho is approximately 2% (Schack and Clemmons 1963).

TABLE 5. ESTIMATED RELEASES OF SILVER DURING MILLING

Ore Type	% of Total Production	Ore Mined (kkg)	Recoverable Ag (kkg)	% Ag Recovery[1]	Total Estimated Milling Loss (kkg)	Estimated Releases (kkg)		
						Air	Land	Water
Ag	46.9	999,670	574	98	11	1[3]	13	1[4]
Cu	31.6	223,147,740	387	91	35	<1	46	–[6]
Cu-Pb-Zn	7.4	3,262,630	91	90	9	<1	3	–[6]
Au/Ag	6.6	669,010	81	90	8	–	–	–
Pb	5.2	7,961,820	64[7]	68 MO	1	–	–	–
				98 Others	1	–	–	–
Au	1.4	3,173,700	17	98	0.4	–	–	–
Old Tailings	0.6	110,270	8	98	0.2	–	–	–
Zn	0.2	1,257,230	2	81	0.4	–	–	–
TOTAL[8]	99.9	240,469,800	1225		66	3	62	1

---

[1] Smith and Carson (1977).

[2] Data not otherwise noted based on emission and recovery figures of Schack and Clemmons (1963). Due to the different data source for these numbers, these columns do not add up to number in Total Estimated Milling Loss column.

[3] Based on amount of ore crushed, 0.75 kg dust/ton ore for Cu, Pb, and Zn processing, and amount of silver in ore. Smith and Carson (1977).

[4] Based on "average" mill water data extrapolated to 1978 production levels (U.S EPA 1975c).

[5] Included in tailing pond discharge listed under land.

[6] Missouri Pb ore accounts for 5.2% of total, Drake (1978 and 1979).

[7] Totals may not add due to rounding.

Source: Drake (1980) unless otherwise noted.

3. Smelting and Refining Containing Silver

a. Overview

Primary smelting separates metals of value from waste minerals present in the ore concentrate (gangue), a step necessary prior to refining. The process used for different ores involves basically the same operations, though the amount of silver discharged varies. Silver recovered as a byproduct from the smelting and refining of copper, lead, and zinc ore concentrate totaled 1180 kkg in 1978. Approximately 510 kkg silver were produced from smelting and refining of silver ore concentrates (Drake 1979). Additionally, 300 kkg of silver ore and concentrates were imported in 1978 (Drake 1979). Processing of these imported materials is included in the amounts for domestic smelting and refining, shown in Table 6.

Secondary smelting is the recovery and refining of silver contained in scrap material and discarded products. Approximately 1150 kkg of silver were produced by this process in 1978. The locations of U.S. smelting and refining facilities are shown in Figure 3.

b. Copper Recovery

Primary copper smelting and refining require roasting of the ore concentrate, reverberatory furnace smelting of the concentrate to form copper matte, oxidation of the matte in converters to yield blister copper, furnace purification of the blister copper and casting of anodes, electrolysis to produce pure copper, and processing of slime residue by hydro- pyro- or electrometallurgic means to recover precious metals (Schack and Clemmons 1963).

Smelters recover an estimated 95% of the copper, silver, and gold initially present in the ore concentrate (Schack and Clemmons 1963). Most silver emitted from smelting and refining operations is lost to the atmosphere as dusts and fumes from roasting and converting processes. Although dusts and fumes are collected and recycled, approximately 8 kkg of silver were emitted to the atmosphere in 1978 (Smith and Carson 1977). Slag from the reverberatory furnace, which contains 1-2% of the silver originally present in the ore concentrate, is discharged to land. An estimated 1 kkg of silver is lost annually to water, mainly through disposal of spent electrolyte solutions used in the refining process (U.S. EPA 1975a). Silver releases from copper smelting and refining are summarized in Table 7.

c. Lead Recovery

Lead smelting and refining involve sintering to agglomerate feed material, smelting to produce lead bullion, drossing the impure bullion to remove copper, and refining by electrolytic or kettle methods (Smith and Carson 1977). Silver is removed at many points during these processes (largely as slags or mattes), but most is recovered in the lead

TABLE 6. SMELTING AND REFINING OF ORES CONTAINING SILVER IN THE U.S., 1978

Source		Amount of Silver (kkg)
Primary Refining (Concentrates & Ores)		
Domestic		1370
Foreign		320
	Total	1690
Ore Type[1]		
Cu Pb Zn		1180
Ag		510
	Total	1690
Secondary Refining		
Old Scrap[2]		1110
Coins		40
	Total	1150
New Scrap[3]		1280
TOTAL NET PRODUCTION		2840
TOTAL PRODUCTION (including new scrap)		4120

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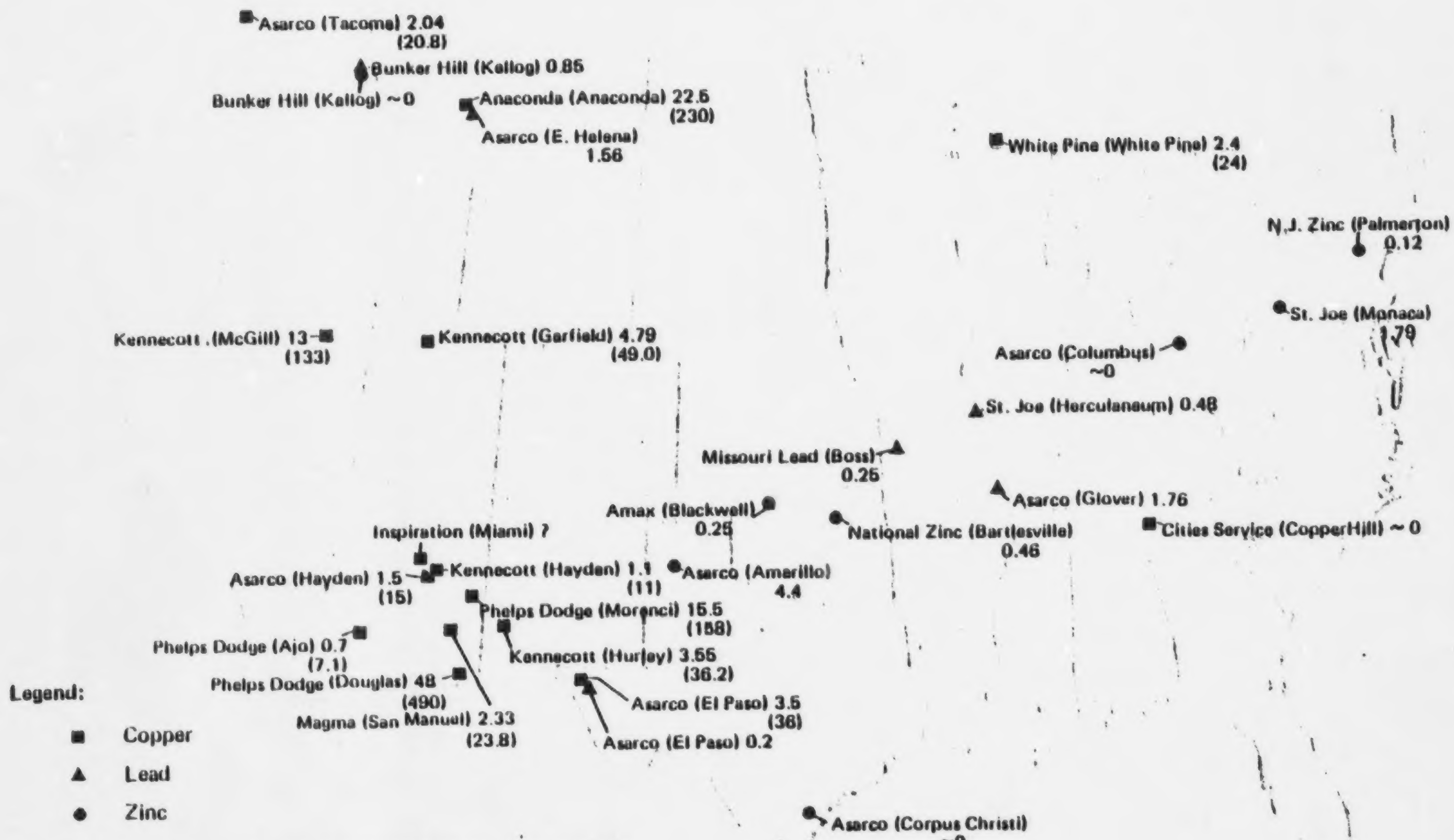
[1] Refinery production by ore type is approximate; Drake (1979) states that 70% of primary refining is attributed to Cu, Pb, and Zn ore.

[2] Old scrap is silver containing material that has moved into commerce as a silver containing product

[3] New scrap is metallic material (bullion) held in stockpiles and eventually recycled at refineries, and is thus not included in this total net production

Source: Drake (1979).


Asarco (Tacoma) 2.04 (20.8)
Bunker Hill (Kellog) 0.85
Bunker Hill (Kellog) ~0
Anaconda (Anaconda) 22.5 (230)
Asarco (E. Helena) 1.56
White Pine (White Pine) 2.4 (24)
N.J. Zinc (Palmerton) 0.12
St. Joe (Monaca) 1.79
Kennecott .(McGill) 13 (133)
Kennecott (Garfield) 4.79 (49.0)
Asarco (Columbus) ~0
St. Joe (Herculaneum) 0.48
Missouri Lead (Boss) 0.25
Asarco (Glover) 1.76
Amax (Blackwell) 0.25
National Zinc (Bartlesville) 0.46
Cities Service (CopperHill) ~ 0
Inspiration (Miami) ?
Asarco (Hayden) 1.5 (15)
Kennecott (Hayden) 1.1 (11)
Asarco (Amarillo) 4.4
Phelps Dodge (Morenci) 15.5 (158)
Phelps Dodge (Ajo) 0.7 (7.1)
Kennecott (Hurley) 3.55 (36.2)
Phelps Dodge (Douglas) 48 (490)
Magma (San Manuel) 2.33 (23.8)
Asarco (El Paso) 3.5 (36)
Asarco (El Paso) 0.2
Asarco (Corpus Christi) ~0
Legend:
■ Copper
▲ Lead
● Zinc

Note: Values in parentheses are estimates of silver emissions in troy oz/day based on data for one smelter: 10.2 troy oz silver/ton particulate emissions.

Source: U.S. EPA, 1974.

FIGURE 3 LOCATIONS OF AND PARTICULATE SILVER EMISSIONS FROM PRIMARY COPPER, LEAD, AND ZINC SMELTERS IN THE U.S., 1974

TABLE 7. ESTIMATED ENVIRONMENTAL RELEASES OF SILVER FROM PRIMARY AND SECONDARY SMELTING/REFINING IN THE U.S., 1978

Process		Estimated Silver Input (kkg)	Silver Production (kkg)	Estimated Silver Releases (kkg)			
				Air	Land	Water	Total
Primary Smelting/ Refining							
	Copper ore	1300	1180	8[3]		<1[4]	8
	Lead ore			2[5]	25[6]	<1[7]	27
	Zinc ore			4[8]	78[7]	1[10]	83
	Silver ore	510	510	5[11]			5
	Total	1810	1690	19	103	2	123
Secondary Smelting/ Refining							
	Silver scrap	1160	1150	7[12]		2[13]	9
	Copper scrap					<1[13]	<1
	Lead scrap			<1[4]		<1[13]	<1
	Total	1160	1150	8		2	10

---

[1] Inputs based solely on addition of emission and production values.

[2] Production data from Drake (personal communication 1980).

[3] Based on 45 mg/kg Ag in particulate emitted (Smith and Carson 1977).

[4] Based on waste effluent concentration of 0.02 mg/l Ag, plant effluent flow rate (U.S. EPA 1979b) and 1978 copper production figures (H. J. Drake, personal communication, 1980).

[5] Assume 45% of silver production is via Pb smelter; 1165 kkg particulates emitted per year containing 0.175% silver (Smith and Carson 1977).

[6] Based on 5% smelting loss, minus estimated air and water emissions (Schack and Clemmons 1963)

[7] Based on an average waste effluent of 0.064 kkg of silver and an approximate flow rate of 1.8 mgd (U.S. EPA 1975a).

[8] Based on 1714 mg/kg Ag in particulate, 7.56 tons particulate/day (Smith and Carson 1977).

[9] Based on 473 mg/kg Ag in retort residue (Smith and Carson 1977). See text.

[10] Based on 1979 EPA Effluent Guidelines data and 1978 production figures (H. J. Drake personal communication 1980).

[11] Assume 1% loss during furnace operations (Smith and Carson 1977).

[12] Assume 1% smelting loss, minus estimated water loss (Smith and Carson 1977).

[13] Based on EPA Effluent Guidelines Data (U.S. EPA 1976).

[14] Based on emission estimates (Smith and Carson 1977).

bullion desilverizing step or as anode slime. Silver contained in mattes or slags may be recycled to a copper smelter. Retorting of the dross from the desilverizing step and oxidation of the remaining lead yields dore metal (94% to 97% silver). Anode slimes are recovered in a similar manner (see Section e.i., Primary Silver Refining).

As in other nonferrous smelting and refining processes, wastes are extensively recycled; the major sources of silver release are from stack gases and slag. On the basis of measurements at lead smelters, an estimated 2 kkg of silver were lost to the atmosphere in 1978 (U.S. EPA 1974). For an average concentration in waste effluent of 0.064 mg/kg silver and an approximate flow rate of 1.8 million gallons per day, an estimated 1 kkg of silver was lost to water (U.S. EPA 1975a). Discharges to land (as slag) are more difficult to quantify. If the overall loss of silver is assumed to be 5%, approximately 25 kkg are lost to land (Schack and Clemmons 1963). Such an assumption seems at least reasonable; in 1974 8.8% of the silver present in Missouri lead concentrates was reported to be lost as slag during smelting and refining operations (Smith and Carson 1977).

d. Zinc Recovery

Primary smelting and refining of zinc ore is by the retort process, or the electrolytic process. Both are efficient for zinc recovery, but since the electrolytic process recovers more precious metals, all new plants use this process (Schack and Clemmons 1963). In either process, zinc concentrates are first roasted in multiple hearth or fluidized bed furnaces to remove sulfur and most of the lead, fluorine, chlorine, and mercury. Particulate emissions are collected and recycled to a lead smelter.

Wastes are in the form of flue dusts (containing approximately 1700 mg/kg silver), lead sulfate residue (~2600 ng/kg silver), and the distillate from zinc reduction. Most of the wastes are presumably recycled within the same process (Phillips 1962; Nauert 1962; Smith and Carson 1977) or, if the quantity of any of the other metals in the waste is high enough, to a processing facility for that metal.

On the basis of a silver concentration of 1700 mg/kg in flue dusts and an emission rate of 6.9 kkg of particulates per day from all zinc operations in the U.S., an estimated 4.3 kkg silver is emitted to the atmosphere annually from primary zinc smelting and refining (U.S. EPA 1974). This estimate is conservative, since approximately 26% of zinc production involved horizontal retorts with uncontrolled emissions (Smith and Carson 1977). The large amounts of silver lost to land are a result of stockpiling of retort residue, which contains as much as 470 mg/kg silver (Smith and Carson 1977). The residue is shipped to a lead smelter when metal concentrations are high enough to warrant recovery (Schack and Clemmons 1963). Silver losses to water from zinc processing are estimated to be 1.2 kkg per year (see Table 7). A survey by the U.S. EPA demonstrated that five out of the six U.S. zinc smelting and refining plants in operation today discharge process water directly; the highest silver concentration, 200 ug/l, was found in leachate effluent (U.S. EPA 1979b).

e. Silver Recovery

i. Primary Silver Refining

In primary refining, silver is recovered from copper refinery slimes (∿1 to 2% silver) and silicate slags (up to 2000 mg/kg silver), in a process involving leaching and roasting to form a matte. This substance is further refined (with sodium carbonate or potassium nitrate) and oxidized to yield dofe metal containing 94-97% silver (Johnson 1967). Then, by use of either the Balbach-Thum or Moebies electrolysis process, the dofe metal is broken down into an anode slime from which silver is collected through leaching or dissolution.

No specific data were found concerning losses to the environment from primary silver smelting and refining. If the silver loss is assumed to be 1%, 5 kkg of silver were emitted to the atmosphere during furnace operations in 1978 (Smith and Carson 1977).

ii. Secondary Silver Refining

Secondary smelting and refining--the processing of silver, copper, and lead scrap--yielded 1150 kkg of silver in 1978 (Drake 1979). Initially, this scrap is segregated into low- and high-grade scrap. Low-grade scrap is mixed with lead scrap and pyrite (an iron-lead ore) and smelted to yield lead bullion. High-grade silver scrap is added to the lead bullion; this mixture is refined to dofe metal.

Few specific data were found concerning releases to the environment from these processes. If 1% of the silver is lost from secondary silver smelters, 6 kkg of silver were emitted to the air in 1978 (Smith and Carson 1977). In 1978, approximately 2 kkg of silver were discharged to water from secondary silver smelting and refining (Table 7), U.S. EPA data concerning wastewater from 24 plants indicated that most of the silver was discharged from disposal of electrolyte solutions (U.S. EPA 1979b).

Other sources of silver discharges to the environment are secondary lead and copper smelters. An estimated 1 kkg of silver was emitted to the atmosphere from secondary lead smelting, on the basis emission data from Smith and Carson (1977) and 1978 production figures. According to U.S. EPA wastewater data concerning the secondary lead smelting industry, disposal of battery electrolyte solutions was responsible for the majority of the estimated 1 kkg silver lost to water. Furnace scrubber effluent and waste electrolyte solutions accounted for most of the estimated 1 kkg silver lost to water from secondary copper smelting and refining (U.S. EPA 1979b). No data are available from which to estimate air emissions from secondary copper smelting.

D. PRODUCTION IN WHICH SILVER IS A BYPRODUCT

1. Overview

Cement manufacturing, combustion of coal and petroleum, and production of iron and steel are all sources of silver emissions. Silver losses from these processes (Table 8), however, do not appear to be significant in comparison with those from milling, smelting, and refining of silver containing ore, concentrates, and scrap.

2. Cement Manufacture

In 1978, 68.6 x 10^6 kkg of cement clinker was produced from approximately 116.8 x 10^6 kkg of raw materials, the majority of which were limestone, clay, shale, and gypsum (see Table 8). The silver content of these materials is 0.07 mg/kg, 0.1 mg/kg, 0.1 mg/kg and .1 mg/kg, respectively. If limestone, clay, shale, and gypsum are assumed to be approximately 70% of all raw materials used in cement manufacture, the silver content in cement is estimated to be 0.3 mg/kg. Table 7 delineates silver discharges to the environment from the cement industry. The major releases are from the kiln, where raw materials are heated, and the dry piling of dust collected from the kiln.

Cement is produced by either a wet method, in which materials are fed to the kiln as a slurry, or a dry method, in which materials are fed in a dry solid form. In 1976, 58% of the cement was manufactured by the wet method, 42% by the dry method (Wingard 1976). If these same proportions are assumed for 1978, 40 to 10^6 kkg cement was produced via wet method and 29 x 10^6 kkg via dry method.

The major source of releases to the environment from cement manufacturing is the kiln. If the silver content of the emissions is the same as that of the charge (0.3 mg/kg) for each kkg of cement produced by the wet method 12 kg particulates are emitted; 40 x 10^6 kkg cement clinker was produced in 1978. If the silver content of the emissions is the same as that of the charge (0.3 mg/kg) less than 1 kkg silver was emitted to the air from cement manufacturing via the wet method. Similarly, for each kkg of cement produced by the dry method, 34 kg particulates are emitted, and 29 x 10^6 kkg cement containing 0.3 mg/kg were produced. Thus less than 1 kkg of silver was emitted to the atmosphere from cement production via the dry method (U.S. EPA 1976b).

3. Combustion of Coal and Petroleum Products

Coal and petroleum contain trace amounts of silver; combustion of these materials necessarily results in environmental silver discharge. Petroleum supplied for use in the U.S. in 1978 total 9.6 x 10^{11}(U.S DOE 1980). If the silver concentration is assumed to be 0.001 mg/l approximately 1 kkg of silver was emitted to the atmosphere from petroleum combustion (Smith and Carson 1977).

TABLE 8. ESTIMATED ENVIRONMENTAL RELEASES FROM PRODUCTION PROCESSES IN WHICH SILVER IS A BYPRODUCT, 1978

Source	Estimated Silver Input (kkg)	Estimated Silver in Product (kkg)	Estimated Releases (kkg)			
			Air	Land	Water	Total
Cement Manufacture	9	5				
wet process			1[1]	1[2]		2
dry process			1[3]	1[4]		2
Petroleum Combustion	1		1[5]			1
Coal Combustion						
bituminous	17[6]		5[7]			5
sub-bituminous	2		1			1
anthracite	1		1			1
lignite	1		1			1
Iron and Steel Manufacturing						
iron production:						
sintering	4	3	1[8]			1
blast furnace	9	8	1[9]			1
steel production:						
open hearth furnace	3	2	1	1		1
basic oxygen furnace	9	3	1	1		1
electric arc furnace	4	8	1	1		1
Iron Foundries			2[10]		neg	2
TOTAL			18	2	neg	20

[1] Assume 39.7 x 10^6 kkg produced, 12 kg particulate/kkg cement produced, and 0.3 mg/kg Ag in particulate (Portland Cement Association, personal communication, 1980, U.S. EPA 1976b; Wingard, 1978).

[2] Assume 39.7 x 10^6 kkg prodcued, 97 kg particulate/kkg produced, and 0.3 mg/kg Ag (Wingard 1978; U.S. EPA 1976b; Portland Cement Association personal communication, 1980).

[3] Assume 28.8 x 10^6 kkg produced, 97 kg particulated/kkg cement produced, and 0.3 mg/kg Ag in particulate, (Wingard 1978; U.S. EPA 1976b; Porland Cement Association personal communication, 1980).

[4] Assume 28.8 x 10^6 kkg produced, 87 kg particulate collected/kkg produced, and 0.3 mg/kg (Wingard 1978; U.S. EPA 1976b; Portland Cement Association, personal communication 1980).

[5] Assume .001 mg/kg Ag concentration and 9.6 x 10^{11}l product supplied for use (Smith and Carson 1977 and U.S. DOE 1980).

[6] Assume 0.04 mg/kg Ag in bituminous coal, 0.02 mg/kg Ag for the remainder (P. Zubovik personal communication, 1980; Assume 74% of coal bituminous, 19% sub-bituminous, 6% lignite, and 1% anthracite (U.S. DOE 1980).

[7] Assume emission factor to air of 0.3 (Slater and Hall 1973).

[8] Assume 32.7 x 10^6 kkg iron production by sintering in 1978, 0.02 kkg particulate emitted/kkg produced, and maximum silver content of 0.1 mg/kg (Desy 1978, J. Copeland, personal communication, 1980). See text.

[9] Assume 79.5 x 10^6 kkg iron production by blast furnace in 1978, 0.42 kg particulate/kkg produced/ and a maximum Ag content of 0.1 mg/kg (U.S. EPA 1978a).

[10] Assume 27200 kkg particulate nationally from cupola (C. Mann personal communication, 1980; 0.08% Ag in emissions (U.S. EPA 1973b). Does not include 112 x 10^6 kkg emissions from non-melting operations.

[11] Negligible. Silver concentration of 0.01 mg/l found in three of 44 waste streams (J. Williams, personal communication 1980).

Coal production in 1978 totaled 5.67 x 10^8 kkg, 76% of which was used to generate electricity. The remainder was used in coke plants, steel mills, and sold to retail dealers. The silver concentration is assumed to be 0.04 mg/kg in bituminous coal, and 0.02 mg/kg in subbituminous coal, anthracite, and lignite. Silver emissions to the atmosphere, as noted in Table 8, are estimated to be 5 kkg for bituminous coal and approximately 1 kkg each for anthracite, lignite, and subbituminous coals. Though silver might also be discharged to ground water supplies as a result of flyash and bottom ash leaching, silver migration is expected to be minimal because of the basic nature of ash.

4. Iron and Steel Manufacture

Manufacture of iron and steel is apparently responsible for small discharges of silver to the environment. Iron is produced by sintering, a process that fuses small ore particles before they are fed to the blast furnace, or by direct reduction in a blast furnace. Steel is produced from open hearth, basic oxygen, or electric arc furnaces. Emission to the atmosphere is apparently the major pathway for silver loss from iron and steel manufacture. Silver, however, is also probably lost in the discarded slag in the same proportion as it is found in the charge.

In 1978, 32.7 x 10^6 kkg iron was produced by sintering (S. H. Desy, personal communication, 1980). On the basis of EPA estimates that 0.02 kkg particulates were emitted per kkg iron produced (U.S. EPA 1978a) and that particulates contain 0.1 mg/kg silver (J. Copeland, personal communication, 1980), less than 1 kkg silver was lost to the atmosphere from sintering. Blast furnace iron production for 1978 totaled 79.5 x 10^6 kkg. An estimated 0.42 kg of particulates were emitted per kkg iron produced (U.S. EPA 1978a). If the silver concentration is assumed to be 0.1 mg/kg, less than 1 kkg silver was emitted to the atmosphere from blast furnace operation.

Steel production via open hearth, basic oxygen, and electric arc furnaces resulted in releases of 27500 kkg, 19500 kkg, and 21800 kkg of particulates, respectively, in 1978 (R. Sevaydarian, Effluent Guidelines Division, U.S EPA, personal communication, 1980). Silver levels in these emissions were less than the 0.1-mg/kg lower detection limit of the analytical technique used. For purposes of estimating the silver content of the particulate emissions, 0.1 mg/kg was used as the maximum silver concentration. Thus, each of the three furnace types emitted less than 1 kkg of silver to the atmosphere.

In 1978, U.S. iron foundries produced approximately 15 kkg of gray, malleable, and ductile iron and steel using pig iron, iron scrap, coke, limestone and silica sand (National Foundry Association, personal communication, 1980). Particulate emissions from the cupola furnace in which iron is melted, were estimated by U.S. EPA to be 27200 kkg (C. Mann, personal communication, 1980). This figure does not, however, include fugitive emissions from non-melting operations such as grinding, operation of cooler ovens, and sand handling estimated to be 112 x 10^6 kkg (C. Mann, personal communication, 1980). Since the ratio of charge materials to the kiln varies widely, as do their silver concentrations, no specific value for the silver concentrations of foundry emissions is available. The U.S. EPA estimated the silver content of cupola emissions to be 80 mg/kg (U.S. EPA 1973b). If these data are used, 2 kkg of silver is estimated to be emitted as particulate matter form cupola furnaces.

Aqueous discharges of silver from iron foundries are negligible. An EPA survey detected silver in only 3 of 44 waste streams sampled; the highest silver concentration was 0.01 mg/l (J. Williams, personal communication, 1980).

E. END USES

1. Overview

The uses of silver are diverse, ranging from photography to cloud seeding. Approximately 5,340 kkg of silver were consumed for end uses in 1978. Statistics for silver consumption by end use are presented in Figure 4; estimated environmental releases resulting from the various uses or operations are summarized in Table 9.

2. Photography

a. Overview

The photographic industry consumed 2000 kkg silver in 1978, or 40% of the total industrial consumption (Drake and Butterman 1979); this sector is the largest single end user of silver.

The principal uses of silver by the photography industry are the manufacture of photographic paper, cloth, film, and plates, X-ray film, and office copying systems. Some substitution of silver will occur in photography and X-ray systems as progress continues with silverless image reproduction, but no significant reduction in the use of silver by such systems is foreseen (Drake 1978).

The use of silver results from the reduction (i.e., development) of exposed silver salts under mild conditions. When exposed to radiation of suitable energy ($\lambda<400$ nm) silver halides are photolyzed to yield silver and halogen. After development of sensitized crystals, the photographic image is "fixed" by removal of any remaining silver salt with a complexing agent, generally sodium thiosulfate, which forms an extremely stable complex with Ag^+ ($\log K = 13.23$). Photographic emulsions are prepared from silver nitrate and sodium or potassium chloride or bromide, in the presence of a colloidial substance, which prevents their coalescence.

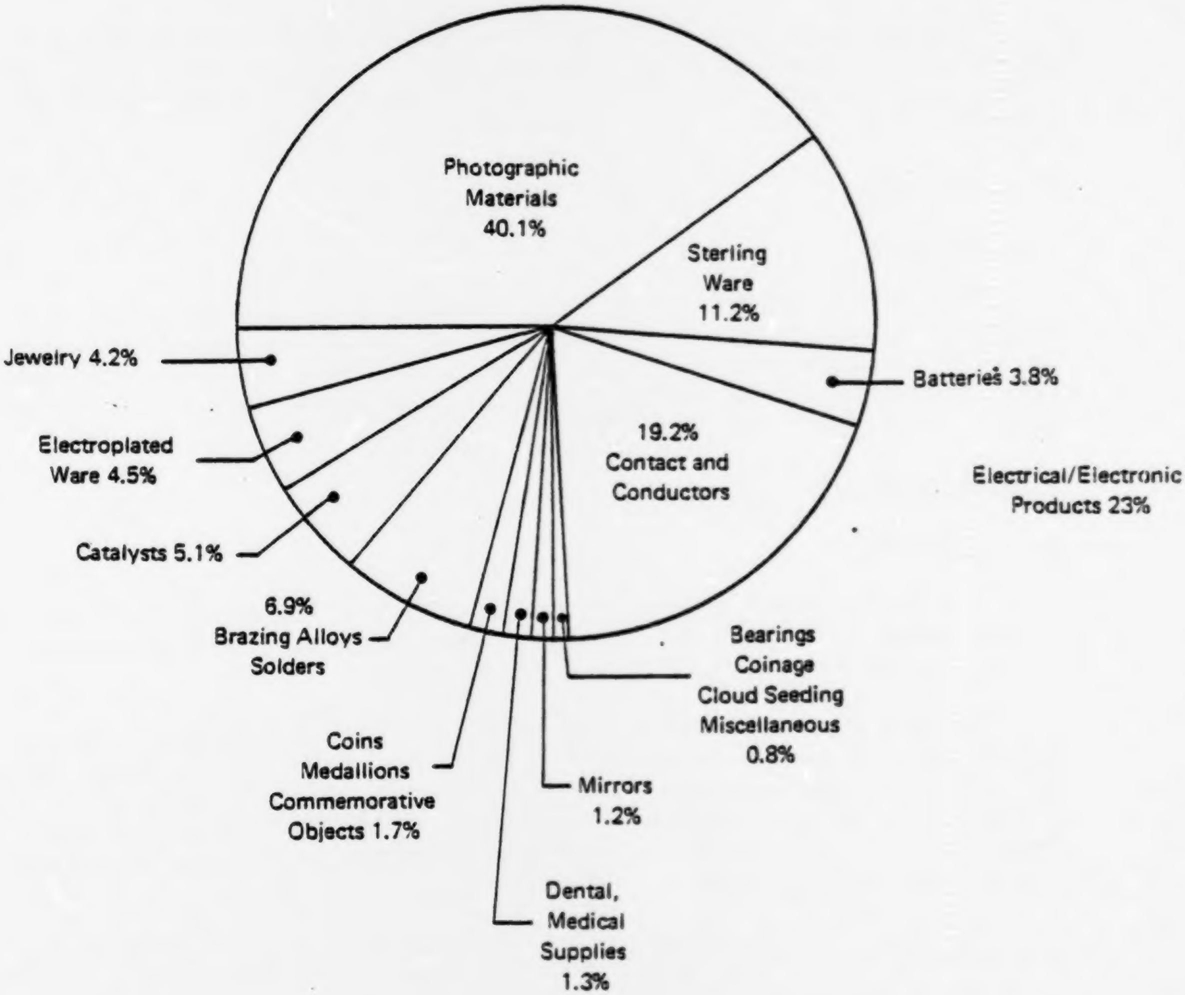


FIGURE 4 DISTRIBUTION OF INDUSTRIAL END USES OF SILVER

TABLE 9. MATERIALS BALANCE FOR END USES OF SILVER, 1978

End Use	Consumption[1] (kkg)	Environmental Release (kkg)		
		Air	Land	Water
Photographic Industries	2000 [2] (1860)	4[3]	630[4]	207[5]
Electrical/Electronic Products				
Batteries[6]	190	-	-	-
Contacts/Conductors	960	21.6[8]	150[9]	-
Sterling Ware[10]	560	1.2	neg	-
Brazing Alloys/Solders	340	2[11]	60[12]	-
Catalysts[13]	260	0.01[14]	-	-
Electro-plated Ware[15]	230	-	-	1
Jewelry[16]	210	0.4	neg	-
Coins, Medallions & Commemorative Objects[16]	90	-	-	-
Dental/Medical Supplies[17]	60	-	-	-
Mirrors[18]	60	0.05	-	-
Bearings[19]	10	-	-	-
Coinage[16]	1	-	neg	-
Cloud Seeding[17]	2	-	2	-
Miscellaneous Uses[20]	30	-	neg	-
TOTAL	5000 (4860)	27	842	208 = 1077

TABLE 9. MATERIALS BALANCE FOR END USES OF SILVER, 1978 (continued)

[1] Figures for 1978 (Drake and Butterman 1979). See Appendix A for 1979 preliminary totals.

[2] Seven percent of the silver-containing photography products are not consumed in the U.S. (Census Bureau, 1976). Therefore, 1860 kkg is actually consumed domestically, contributing to environmental releases.

[3] $AgNO_3$ production emissions are assumed to be negligible because an enclosed reaction vessel is used, fumes are scrubbed, and all byproduct streams are reused (Guccione 1963). Smith and Carson (1977) use a 1928 figure of 0.2% silver loss in manufacturing of photographic products (Addicks 1940). The 4 kkg shown is a GCA (U.S. EPA 1973b) unsubstantiated estimate, extrapolated to 1978, for emissions from silver recovery.

[4] Smith and Carson (1977), U.S. EPA (1973b) and Schack and Clemmons (1963) estimates, extrapolated to 1978; assume 50% silver recovery (35% by precipitation, 15% by incineration) from amount used in photographic materials and 90% of silver going into fixing baths: 840 kkg with 75% estimated to end up in sewage sludge, 25% remaining in water (U.S. EPA 1980). Of the 840 kkg, 540 kkg come from larger, professional photoprocessors (see Table 10), with silver recovery practiced on at least some processes, and the rest from amateurs and hobbyists (Smith and Carson 1977).

[5] Based on calculations in following section. At least 88 kkg of this amount goes to POTW's (from producers) and up to 119 kkg to surface water and POTW's.

[6] Unsubstantiated discharge estimate from GCA (U.S. EPA 1973b), for sintering, electrolytic processes, and chemical losses: 0.03 kkg.

[7] Virtually no silver oxide or sulfide should escape enclosed contacts or make-and-break switches.

[8] Based on GCA (1973) and estimate of atmospheric emission during spray painting of conductors adapted for 1978 consumption (ADL estimate 1980) is $\sim$0.3 kkg. A GCA-derived estimate for atmospheric release of contacts eroding over time (average lifetime = 20 years); estimate applies to 5% of all contracts in use) is 21.3 kkg.

[9] Land: discarded home appliances (Smith and Carson 1977). Attrition rate of contacts depends on number and severity of duty cycles.

TABLE 9. MATERIALS BALANCE FOR END USES OF SILVER, 1978 (continued)

[10] GCA (U.S. EPA 1973b), unsubstantiated discharge estimate, primarily aerosols from buffing and polishing operations, 0.006 kkg. Based on estimate by Smith and Carson (1977), 0.2% loss of consumption during manufacture of sterling ware and assuming all releases are to air.

[11] GCA (U.S. EPA 1973b) estimate: 1% of the silver emitted as fume, 50% of this 1% is controlled during use. GCA (U.S. EPA 1973b), estimate for loss during production of alloys and solders: 0.005 kkg. Smith and Carson (1977) conclude little uncontrolled silver emissions, strictly an occupational hazard as an aerosol.

[12] Land: in discarded home appliances (Smith and Carson 1977).

[13] Principal uses: formaldehyde and ethylene oxide production.

[14] Based on estimate by Smith and Carson (1977) for aerosol emission, adapted for 1978 consumption (ADL estimate 1980).

[15] Electroplating Point Source Category: 9400 firms, 3000 of which are independent job shops (metal finishing as their primary line of business, as opposed to "captive"). Based on a sampling of the industry (13.4% of total) by Hamilton-Standard (1980), then approximately 700 plants, total, conduct silver-plating. This can be broken down into 269 job shops and 433 captive operations. Based on Versar estimates (1980), the flow rates for job and captive shops are 32,300 gal/day and 277,000 gal/day, respectively. Hamilton-Standard (1980) estimates mean raw wastewater concentrations of 0.38 mg/l and 0.83 mg/l, respectively. Discharges are assumed to occur 250 days/year. Total annual discharges of silver are 0.003 kkg by job shops and 0.009 kkg by captives. In addition to these numbers, a chemical and liquid spill estimate of 0.008 kkg (U.S. EPA 1973b) is added to give a total of 0.10 kkg of silver released. More than 50 % of this amount is released to POTW's (Hamilton-Standard 1978) but because the total number is so small, all is assumed discharged directly to water.

[16] Based on estimate by Smith and Carson (1977) of 0.2% loss of consumption during manufacture of jewelry and coins and assuming all releases are to air.

TABLE 9. MATERIALS BALANCE FOR END USES OF SILVER, 1978 (continued)

[17] Dental/Medical and Cloud Seeding considered "dispersive" uses; that is, exposure to silver is a normal consequence of use. Dental/Medical includes non-medical antimicrobial uses in food, drinking water and swimming pools. GCA (U.S. EPA 1973b) discharge estimate for preparation of materials: 0.003 kkg. In cloud seedings, a large majority of the silver should end up in water or land. Release have been all allocated to land. Measured mean rainwater [Ag] during seeding - surface: 6×10^{-11} g/ml, cloud base: 4×10^{-9} g/ml (Wisniewski et al. 1976).

[18] In solar applications, 3 Quads (10^{15} Btu, 2.5×10^{14} Cal)/yr is the national goal for the year 2000. 3 Quads = 8.4×10^{8} m^2 surface area; 10^{-6}m = silver thickness of mirrors; 10.5×10^{6} g/m^3 = silver density. Thus, by 2000 9000 kkg of silver could be used annually for solar mirrors. GCA (EPA 1973b) unsubstantiated discharge estimate for spraying of mirroring solutions: 0.05 kkg. Electroless silver solutions must be neutralized before disposal as the silver-amine complex is explosive.

[19] GCA (U.S. EPA 1973n) unsubstantiated discharge estimate: "0.06 kkg for bearings and lubricants, loss of flake silver lubricant in use"; the amounts of metals in jet engine lubricating oils are criteria for changing the oils.

[20] Includes Ag-bearing copper, Ag-bearing lead anodes, ceramic paints, etc. Discharge estimate is unsubstantiated.

The major photographic supply manufacturers number approximately 134 (U.S. EPA 1980) and are located in the northeast corridor, particularly in New York and New Jersey. These include Kodak, GAF, Englehard, and 3M, along with DuPont in Wilmington, Delaware. Silver nitrate is also manufactured in Illinois by D.F. Goldsmith Chemical and Metal, Apache Chemicals and NL Industries, Goldsmith Division. Photoprocessing, in contrast to manufacturing, is widespread throughout urban centers in the U.S.

As shown in Table 9, the photographic industry releases an estimated 4 kkg to air, 630 kkg to land, and 207 kkg to water each year. The silver-bearing wastes generated by the photographic industry result from consumption as well as manufacture of the photosensitive products. Liquid wastes are chiefly spent fixing, bleaching, and post-fix washing solutions released during manufacturing and photoprocessing operations. Solid wastes include spoiled, out-dated, developed and undeveloped negatives and print paper, as well as contaminated emulsions and scrap trimmings. During the manufacture of emulsions, silver discharge is probably negligible, due to the fact that an enclosed reaction vessel is used, fumes are scrubbed, and all byproduct streams are reused (Guccione 1963).

The following discussion summarizes environmental releases of silver by photographic equipment and supply manufacturers, commercial photoprocessors, and amateur photoprocessors. The available data concerning environmental releases by the photographic industry are not consistently disaggregated into the three industry categories mentioned above. Therefore, aqueous discharges by the three subcategories are first discussed and then releases to air and land are summarized for the photography industry as a whole.

b. Production

Silver is discharged to both surface waters and POTW's by producers of photographic products. Photographic aqueous point sources have been categorized by the Effluent Guidelines Division (U.S. EPA 1980) into the following groupings:

(1) Silver Halide Subcategory

(2) Diazo Aqueous Subcategory

(3) Photographic Chemical Formulation Subcategory

(4) Thermal Product Subcategory Process

For each subcategory, Table 10 summarizes plant flow rates and typical Ag concentrations in effluent from data collected in the Effluent Guidelines Division sampling program.

Major producers of photography products are expected, due to economic incentives, to recover a large fraction of the silver contained in solid and liquid wastes (U.S. EPA 1973b, Schack and Clemmons 1963). However, quantifying the percentage recovery and the amount of silver actually released to the environment is difficult due to lack of information for all plants. The usual system for in-house treatement and recovery is chemical precipitation and sedimentation, which results in a large fraction of silver ending up in sludge. At least 20 photographic producer plants currently use this technique and 18 additional plants use settling or clarification (U.S. EPA 1980). The effectiveness of the treatment in removing silver from raw wastewater is variable. Due to a lack of information on current silver recovery practices by the remaining producers, and efficiencies of treatment for silver by the photographic industry, the estimates of total discharges are based on levels in raw wastes. Figure 5 illustrates silver recovery from photographic wastes.

In order to estimate annual releases to aquatic systems the following assumptions were made:

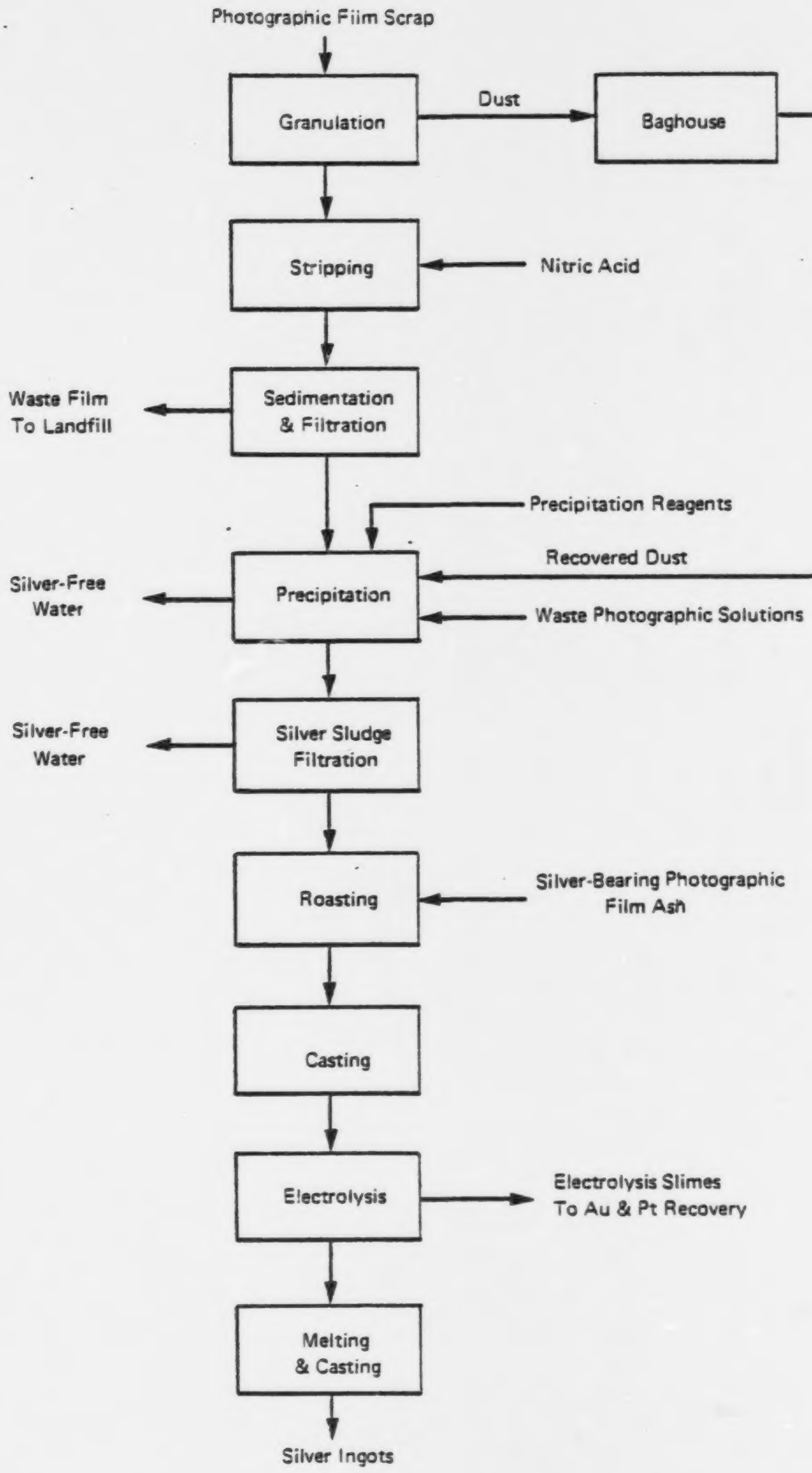
- The mean raw wastewater concentration (usually greater than median or flow-adjusted concentration) was representative of all plants and provided a reasonable worst-case estimate (Table 10);
- Discharge occurred 365 days per year;
- Discharges from sources for each subcategory contained silver originating only from the subcategory for that process. In other words, each plant and/or discharge of wastewater is discrete and uses only one process.

Table 11 shows the magnitude and distribution of the estimated aqueous discharges of silver to surface water and POTW's by each photographic industry subcategory.

c. Professional Photoprocessing

The larger photoprocessors of film are estimated to recover, by in-house refining or shipment to commercial refiners, approximately 50% of silver in liquid and solid wastes (U.S. EPA 1973b, Schack and Clemmons 1963). The usual system for in-house silver recovery of liquid wastes (fixer and bleach) is an electrolytic primary unit, followed by a metallic replacement tailing unit. Silver removal efficiencies of over 95% are possible when the two methods are used in series (U.S. EPA 1979c).

The approximately 10,620 professional photoprocessing establishments in the U.S. range in processing capacity from less than 23 m^2 to greater than 47,000 m^2 of film annually. Table 12 presents estimated annual discharges to water by size of establishment. The total annual release is approximately 30 kkg on the basis of Effluent Guidelines (U.S. EPA 1979c)


Photographic Film Scrap
Granulation
Dust
Baghouse
Stripping
Nitric Acid
Waste Film To Landfill
Sedimentation & Filtration
Precipitation Reagents
Recovered Dust
Silver-Free Water
Precipitation
Waste Photographic Solutions
Silver-Free Water
Silver Sludge Filtration
Roasting
Silver-Bearing Photographic Film Ash
Casting
Electrolysis
Electrolysis Slimes To Au & Pt Recovery
Melting & Casting
Silver Ingots

Source: U.S. EPA, 1979b.

FIGURE 5 FLOW DIAGRAM FOR SILVER REFINING FROM PHOTOGRAPHIC WASTES

TABLE 10. SILVER LEVELS IN THE WASTEWATER OF PHOTOGRAPHIC MATERIAL AND EQUIPMENT PRODUCERS

Subcategory	No. of Plants	Average Daily Flow (l/day)	Silver Concentration in Wastewater (mg/l)				Flow-Proportioned Concentration	No. Observations (Positive/Negative	% Released To	
			Minimum	Maximum	Mean	Median			POTW	Surface Water
Silver Halide	22	804013	0.39	36.88	14.11	12.85	9.	14/0	64	33
Diazo Aqueous	32 (+5 that do not discharge)	4459	0.00124	0.00271	0.00298	0.00198	0.00191	2/14	71	5
Photographic Chemical Formulation	59 (+8 that do not discharge)	66207	0.00444	0.063	0.02845	0.02900	0.01195	9/8	39	60
Thermal Product	10	7986	0.04191	0.61906	0.28074	0.18126	0.25543	3/6	99	0

Source: U.S. EPA (1980).

TABLE 11. RELEASES OF SILVER TO WATER BY DIFFERENT PHOTOGRAPHIC INDUSTRY SUBCATEGORIES

Subcategory	Total Annual Load For All Plants (kkg)[1]	Load To POTW'S	Load To Surface Water	Other
Silver Halide	91	58	30	3
Diazo Aqueous	8	6	0.4	1.6
Photographic Chemical Formulation	40	16	24	1
Thermal Product	8	8	0	1
TOTAL	147	88	54	5

---

[1] Estimated by multiplication of mean silver concentration in raw wastewater x daily flow x 365 days/year x number of known discharging plants.

TABLE 12. TOTAL ANNUAL PRODUCTION AND SILVER AQUATIC DISCHARGES OF PHOTOPROCESSING ESTABLISHMENTS BY PROCESSING CAPACITY

Processing Capacity ($10^3 m^2$/yr)	No Establishments	Total Production[1] ($10^6 m^2$/yr)	Silver Discharges[2] To Water (kkg/yr)
<23	9,900	19	13
23 - 35	150	3	1
35 - 47	50	4	1
<47	520	138	35
TOTAL	10,620	164	50

---

[1] (T. Dufficy, personal communication, 1980).

[2] Estimates are based on (1) 0.68 kg/$10^3 m^2$ and 0.26 kg/$10^3 m^2$ Ag discharge from plants with Ag recovery on some or all processes, respectively (U.S EPA 1979c), and (2) the assumption that smaller processing establishments (i.e., 23 x $10^3 m^2$/yr) are more likely to use Ag recovery on only some of the processes.

data and the assumption that waste recovery at smaller establishments is less efficient than at larger plants.

d. Amateur Photoprocessing

Amateur photographers with home darkrooms are most likely to discharge their spent fixing solutions and other aqueous waste directly down the drain without treatment. If one assumes that most home developers live in urban areas, most of this amount most probably goes to POTW's and not directly to surface water. Table 13 estimates the annual discharges of silver to water from this source. The amount discharged is relatively minor, 15 kkg, compared with larger operations, primarily because of the relatively small amount of film developed by amateurs.

e. Atmospheric and Land Releases by the Photographic Industry

The photogrphic industry, both producers and processors, also release silver to the atmosphere and land in waste material. Air emissions from silver recovery of solid waste by incineration of film scrap are estimated to be 4 kkg per year (U.S. EPA 1973b). Releases to land are in the form of sludge from in-house wastewater treatment processes and film scraps and are estimated to contain 630 kkg of silver each year. Both estimates are described in greater detail in Table 9.

f. Total Discharges by the Photographic Industry

Table 14 summarizes the estimated total discharges to the environment by the photographic supplies producers, by small and large photoprocessors, and by amateur photographers. The total is approximately 840 kkg per year and comprises 40% of the total annual consumption of silver by the photographic industry in the U.S.

It should be re-emphasized that the estimated aqueous discharge for photographic producers is based on raw waste concentrations. Assuming treatment of the waste stream by precipitation/sedimentation techniques at 100% efficiency, and practice of this technique by 15% of the industry (20 out of a total of 134 plants), then the direct aqueous discharge would be reduced to 46 kkg annually. However, there is not enough complete information on the total industry to provide an understanding of the effectiveness of recovery practices . As a conservative estimate, raw wastewater levels were used and the silver contribution of the photographic industry is perhaps somewhat overestimated.

3. Other Uses

a. Contacts and Conductors

Manufacturers of electrical contacts and conductors consumed 960 kkg of silver in 1978 (Drake and Butterman 1979). Silver is the most common material in make-and-break contacts, the primary uses of

TABLE 13. ESTIMATED ANNUAL AQUATIC DISCHARGES OF SILVER FROM HOME DARKROOMS

(1) Category	(2) No. of Units x 10^6	(3) No. of sq. ft. x 10^6	(4) Amt. of Ag Recoverable per 10^3 units (Troy oz)(4)	(5) Average Amt. Ag per 10^3 units (Troy oz)
B & W. print paper sq. ft.	120[1]	120	3.2 - 4.3	3.75
Color print paper Sq. ft.	8[1]	8	2.3 - 2.6	2.45
Color reversal paper sq. ft.	1[1]	1	2.5 - 2.8	2.7
B & W film rolls	5-10[1 2]	0.75 (.5-1)	3.3 -13.2	6
Color film rolls	1[2]	0.075 (.05-1)[3]	12 - 23	15

[1] Arthur D. Little, Inc., estimate.

[2] Arthur D. Little, Inc., estimate.

[3] Calculated - 28 rolls of 36 Exp. 35 mm film/sq. meter or 2.8 rolls/sq. ft. = 0.36 sq. ft./roll. A rolls more than offset by large format film, then 0.5 sq. ft./roll.

[4] Eastman Kodak (1977).

TABLE 14. OVERALL ENVIRONMENTAL RELEASES OF SILVER BY THE PHOTOGRAPHIC INDUSTRY, 1978

	Discharges (kkg)			
Source	Surface Water	POTW's	Air[1]	Land[1]
Production	54[2]	88[2]	4	630
Professional Processors	50[3]			
Amateurs	15[4]			
TOTAL	119	88	4	630

---

[1] Air and land emissions are combined for all industry categories; see preceeding section e.

[2] See Table 11.

[3] See Table 12; these releases may also include discharges to POTW's.

[4] See Table 13; these releases may also include discharges to POTW's.

which are in automotive parts, appliances, motor controls, communications and electronic components such as relays, resistors, switches, etc. There are three classes of silver contacts, depending upon the form of silver used: pure silver or alloys (75-99.9% Ag), silver with semi-refractory elements (40-99.3% Ag, most commonly AgCd)), and silver with refractory constituents (Ag-WC, 40-65% Ag or Ag-W, 27.5-90% Ag).

Electrical contacts in discarded home appliances account for a large fraction of silver disposal onto land. Schack and Clemmons (1963) estimated that about 40% of the total silver used in production of alloys and electrical products is returned to refineries for processing and reuse (Schack and Clemmons 1963). The remainder (60%) is too widespread among various end uses to be recovered economically. On the basis of 1978 silver consumption by this industry, an estimated 150 kkg of silver in appliances, demolished buildings, etc. is deposited in landfills. In that contacts and make-and-break switches are enclosed systems, attrition is assumed to contribute a negligible amount of aerosol silver to the environment.

b. Batteries

The amount of silver used for batteries in 1978 was 190 kkg (Drake and Butterman 1977). The major use of silver batteries is in defense and aerospace applications where space is at a premium (e.g., submarine propulsion, missiles, satellites, space vehicles, and in military portable communications equipment). Silver-containing batteries are also used commercially in hearing aids, electronic watches, photoelectric exposure devices, portable equipment, and small appliances.

Approximately 0.03 kkg of silver are estimated to be lost each year through sintering, electrolytic forming processes, and chemical losses in washing and rinsing steps of storage and primary battery production (U.S. EPA 1973b). Most of the silver (mainly silver oxide) is reported to be recovered from wastewater treatment sludge, rejected cells, and scrap cells and then recycled (U.S. EPA 1975d). Thus information concerning this industry indicates that discharges are negligible.

c. Jewelry, Sterling Ware, Collector Pieces, Government Coinage

As the manufacture of jewelry, sterling ware, collector items and coins utilizes similar production processes, such processes are considered as a single category of sources. Total silver consumption for this group in 1978 was 860 kkg: 210 kkg for jewelry; 560 kkg for sterling ware; 90 kkg (1.8%) for coins, medallions and commemorative objects; 1 kkg (0.02%) for coinage. Shavings and dust that settle from grinding, buffing, and polishing operations are recycled by sweeping. Therefore air emissions are probably only an occupational hazard. The jewelry industry utilizes silver in electroplating of base metals or plastic, fabrication from refinery forms, or incorporation into pieces as solder, alloys and inlays. Sterling flatware and holloware are the primary uses of sterling silver. GCA (U.S. EPA 1973b) estimates that 0.006 kkg silver is lost annually from buffing and polishing of sterling and jewelry.

Other uses include collector arts such as commemorative medals and medallions, souvenir plates and bars, etc. Consumption of silver in metal currency dropped sharply when the Coinage Act of 1965 eliminated silver from dimes and quarters and reduced the amount in half-dollars to 40%. Since that time, the trend has been to substitute alloys and less costly metals for silver, with the exception of special memorial coins, such as the Eisenhower dollar.

d. Brazing Alloys and Solders

Production of silver brazing alloys and solder used 340 kkg of silver in 1978 (Drake and Butterman 1979). Brazing is distinguished from normal soldering in that relatively infusible alloys are used, brazing temperatures (315-815°C) are higher than soldering temperatures (175-315°C), and brazing alloys contain up to 93% silver, while solders contain 35% silver or less.

The brazing and soldering processes have similar applications (in approximate order of importance): air conditioning and refrigeration (copper tubing seals), plumbing and heating (industrial and commercial piping), automotive parts, aircraft and aircraft engines, and electrical appliances. Other applications of brazing alloys are shipbuilding, motors and generators, electronic components, and silverware and jewelry. Solders are also used in food service and processing utensils.

GCA (U.S. EPA 1973b) estimated that 1% of the silver used for the alloys and solders is emitted to the air as fumes during soldering operations, and that one-half of this 1% is controlled, most likely through the uses of fluxes and controlled atmospheric furnaces. On the basis of these assumptions, approximately 2 kkg were released to the atmosphere in 1978. Silver lost from production of alloys and solders has been estimated to amount to 0.005 kkg annually (U.S. EPA 1973b). Most of the brazing alloys and solders, however, are lost in land disposal of home appliances and scraped, non-recycled automobiles. On the basis of amount of silver in household appliances, the number of appliances sold each year, and the number of discarded appliances in 1978 (Smith and Carson 1977), an estimated 60 kkg of silver were discharged and disposed of in landfills; an additional 10 kkg was recycled in steel scrap.

e. Catalysts and Olefin Separation

The production of silver catalysts accounted for 260 kkg silver in 1978 (Drake and Butterman 1979). Of the many silver-catalyzed reactions, only oxidation of ethene to ethylene oxide and methanol to formaldehyde use significant amounts of silver as catalysts. Silver is reported to be used for a third process, oxidation of ethylene glycol to glyoxal, but specific data are unavailable.

Ethylene oxide production for 1978 was approximately 2.3 x 10^6 kkg (U.S. ITC 1979). Ethylene oxide plants are located primarily on the Gulf Coast or in Puerto Rico, near supplies of ethene. Ehtylene oxide is produced in the United States exclusively by oxidation of ethene in the vapor phase at 250°C. There are two variations to this process based upon whether air or oxygen itself is used as the oxygen source. In the air oxidation process, the catalyst charge (10-15% silver) is 1.7 kg (0.2 kg silver) per kkg of ethylene oxide capacity. This catalyst is generally removed and regenerated after 18 months of use. In oxygen plants, the catalyst charge is two to three times larger. but its life is prolonged. Most ethylene oxide producers manufacture their own catalysts; two exceptions however, are those plants that use either the Scientific Design process (supplied by Scientific Design's Catalyst Development Corporation) or the Shell process (supplied by Harshaw Chemical Company).

A second important use of silver is production of formaldehyde via oxidation of methanol at approximately 450° to 600°C. The silver catalyst is comprised of high-purity (>99.95) silver in the form of silver needles or gauze. The catalyst charge is regenerated by heating to temperatures sufficient to remove carbonaceous deposits, treating with concentrated hydrochloric acid, removal of the resultant silver chloride with ammonium hydroxide, and electrolizing twice. Catalyst life is reported to be on the order of 6 months to 1 year (Smith and Carson 1977).

A second general application of silver as a catalyst is the separation of olefin mixtures, based upon the formation of complexes of hydrocarbons and silver salts such as nitrates, perchlorates, and fluoroborates. Both liquid and solid phase systems are known (Smith and Carson 1977). The extent to which such systems are used, however, is unclear in that no specific data are available.

No specific data regarding silver loss from catalyst attrition, preparation, or regeneration, are available. On the basis of U.S. EPA estimates (1973b), and the quantity of silver used for catalyst preparation in 1978, 7 kg of silver are estimated to be discharged annually.

f. Electroplating

Silver electroplating is used in a wide variety of products: silverware, bearings, chemical and food processing equipment, electrical machinery, jewelry and decorative art. The Bureau of Mines (Drake 1978) data are given for one major use category, electroplated ware. In 1978, the industrial consumption of silver for electroplated ware was 230 kkg (Drake and Butterman 1979).

The silver plating process is basically performed in three steps: pre-treatment, plating, and post-treatment. First, strike solutions low in silver (1.5-5g concentration AgCN/1) are used to prevent an immersion deposit of silver precipitates. This is followed by plating in a more concentrated bath (30-50g AgCN/1) until the desired thickness is obtained (Lowenheim 1980 and F.A. Lowenheim, personal communication, 1980). Post-treatment with chromate coatings is sometimes employed, to reduce silver tarnishing.

Coatings other than those electroplated include paints (containing 50% to 60% silver) which are used for solder bonding to nonconducting and nonmetallic surfaces, decoration of porcelain and glass, and formation of conductive surfaces on nonconductors. Upon firing of the paints, silver loss is approximately 33% (based upon limited data)(Smith and Carson 1977).

The silver wastes generated in the production of silver-plated tableware are spills of silver-rich electrolyte, dilute wash solutions, and spent electrolyte. Waste plating solutions generally contain 250 mg/1 Ag^+ and the rinse water may contain 50-250 mg/1 (Smith and Carson 1977). Silver-bearing solutions are usually brought together as mill waste and processed to precipitate (or otherwise recover) the silver and oxidize the CN before discharge as a plant waste.

Approximately 36 independent electroplating job shops and 57 captive shops conduct silverplating (Hamilton-Standard 1980). In a small survey of electroplating shops, the median raw wastewater concentration of silver was 0.83 mg/1 in captive and 0.38 mg/1 in independent job shops (Hamilton-Standard 1980). Based on average flow data (Versar, Inc. 1980) and assuming discharge of 250 days/year, a total of approximately 0.09 kkg silver is annually discharged to water. In addition, GCA (U. S. EPA 1973b) estimates that 0.008 kkg of silver is lost annually from chemical and liquid electroplating spills. The estimates are described in greater detail in Table 9. Releases to land and air are assumed to be negligible because of the nature of electroplating operations.

g. Dental, Medical, and Non-medicinal Antimicrobial Uses

Silver consumed in dental, medical and antimicrobial products in 1978 amounts to 60 kkg, or 1.2% of the total (Drake and Buttermore 1979). These uses, in contrast to uses previously described, represent "dispersive" applications; that is, exposure to silver results as a normal consequence of use. Emissions from preparation of these supplies (e.g., melting, casting and cleaning in the manufacture of amalgam alloys) are estimated to be 0.003 kkg/yr (U.S. EPA 1973b).

Amalgam alloys for dental fillings contain 67-70% silver; however, after the alloys have been mixed with mercury for actual application of the filling, the concentration is closer to 33% silver (Smith and Carson 1977). Other dental uses include solders, wires, and local application of ammoniacal silver nitrate to arrest dental decay.

Silver nitrate also has medical applications. Aqueous solutions of 0.01-0.1% silver nitrate are effective antiseptics; compresses soaked with 0.05-0.1% solutions can be applied to severe burns; and highly corrosive 10-20% solutions are applied locally to remove warts (Tischer 1969). Metallic silver is used for prosthetic devices and/or splints, and in electrodes to record brain or heart function.

Silver may also be used in water disinfection systems because of germicidal activity. Although silver has been widely used in Europe as a disinfectant, the extent of such use in the U.S. is unknown. Current applications may include swimming pool disinfection.

h. Mirrors

In 1978, 60 kkg of silver were consumed in electroless plating of mirrors (Drake and Buttermore 1979). The primary difference between electroless plating and electroplating is that in the former, the electrons for reduction are supplied by a chemical reducing agent in solution, rather than as applied potential. Silver mirrors are used for decorative purposes and optical instruments, and their use could become significant as solar energy is developed (see Table 9). GCA (1973) estimated an annual emission to the atmosphere of less than 0.05 kkg of silver from "spraying of mirroring solutions."

i. Bearings

Ten kkg of silver were used in the manufacture of bearings in 1978 (Drake and Buttermore 1979). The principal method of bearing manufacture is to electroplate silver onto steel and machine to size, then to plate a lead-tin overlay. Representative applications of silver-plated bearings are rotor bearings, high-temperature bearings, and self-lubricated bearings. GCA (U.S. EPA 1973b) estimate that approximately 0.06 kkg silver is lost from bearings as flake silver in lubricants annually. Smith and Carson (1977) point out that silver is often measured in used jet engine lubricating oils, as the concentration of metals present is a criterion for changing the oils.

j. Cloud Seeding

Silver iodide has long been favored as a seeding agent for ice nucleation in supercooled clouds, the goal being enhanced cloud growth and increased precipitation; however its use is decreasing. Operational and research cloud seeding operations accounted for 2 kkg silver in 1978 or approximately 0.03% of the total industrial consumption (National Oceanic and Atmospheric Administration 1978). The largest national weather modification project is devoted to augmenting the Colorado River Basin snowpack.

The fate of silver iodide used as a seeding agent is relatively well defined; virtually all of the 2 kkg of silver dispersed is contained in rainwater or snowfall to surface water and land. Wisniewski et al. (1976), in a review of a 1973 Florida seeding experiment, reported that silver concentrations on the order of 10^{-11} ug/ml and 10^{-9} ug/ml were found in surface and cloud base rainwater, respectively.

k. Miscellaneous Uses

In 1978, approximately 30 kkg of silver (0.6% of the total) were consumed in a myriad of minor uses (Drake and Buttermore 1979). The Bureau of Mines (Drake 1978) lists these as "silver-bearing copper, silver-bearing lead anodes, ceramic paints, etc." Smith and Carson(1977) include additional applications, such as rocket propellants ($AgClO_4$), hair colorings ($AgNO_3$) solutions, and nuclear reactor rods (Ag-Cd-In alloy). Most silver compounds are prepared from silver nitrate. Unlike other industrial chemicals, the numerous silver compounds are offered on the market in small quantities, generally of high purity. No estimates of emissions from these sources are available, except that approximately 0.3 kkg is lost, probably to the atmosphere, from spray painting of electrical conductors (e.g., ceramic paints) (U.S. EPA 1973b).

F. MUNICIPAL DISPOSAL

This section deals with the ultimate disposition of silver discharged to municipal waste facilities: publicly-owned treatment works (POTWs) and urban refuse landfills or incinerators. For some sources, the estimated amounts of silver involved overlap the estimates of releases by silver consumers and/or producers. For many industry categories, it was not possible to determine what portion of aqueous discharges were to POTWs and what portion of land disposal was to urban refuse landfills. Therefore releases from POTWs and urban refuse landfills have not been combined with other releases from anthropogenic sources shown previously in Table 2 in order to avoid double counting. A summary material balance for POTWs and refuse is given in Table 15.

1. Publicly-Owned Treatment Works

Silver loading to POTWs is largely dependent upon the type of industry in a particular municipal area. A framework for calculating the total silver flow through the nation's POTWs (see Table 15) is provided by data from a recent U.S. EPA study. A materials balance of silver at the treatment plants can be constructed by use of a total POTW flow of approximately 10^{11}l/day (U.S. EPA 1978b) and median values of 0.008 mg Ag/l (influent) and 0.002 mg Ag/l (effluent) (see Table 16). For purposes of these calculations, influent and effluent flow rates are assumed to be equal, i.e., water loss from sludge removal and evaporation are assumed to be minimal. The amount of silver in sludge is assumed to be the difference between the silver in the influent and in the effluent since losses of silver to the air are assumed to be negligigle.

TABLE 15. SILVER MATERIALS BALANCE FOR POTWs AND REFUSE, 1978

Source	Input	Environmental Releases (kkg/yr)		
		Air	Land	Water
POTW	290[2] 143[4]	neg[1]	220[2] (40)[3] 107[4]	70[2] 36[4]
Urban Refuse				
Incineration	70[5]	10[6]	60[7]	neg[8]
Landfill	310[9] 460[10]		310[9] 460[10]	

---

[1] Engineering judgment, Acurex Corp.

[2] Figures calculated from U.S. EPA data (see Table 12) based on 10^{11} l/day total POTW flow and median values for; influent Ag concentration = .008 mg/l; effluent Ag concentration = .002 mg/l. For land value, sludge is difference between influent and effluent loads and, therefore, includes recycled sludge. Effluent flow equals influent flow. Air emission assumed to be negligible.

[3] A second method of calculation based on 6×10^6 dry kkg sludge produced/yr (U.S. EPA 1979a), wet sludge ~95% water by weight, 0.368 mg/l Ag in wet sludge (see Table 12), and assume 1 liter wet sludge has same density as 1 liter of water (1 kg). Wet sludge flow rate = $\left(\frac{6 \times 10^6}{.05}\right)$ (11/kg) (1 kg/10^3 kkg) = 1.1×10^{11} l/yr.

[4] Non-air discharge for photography (see Table 9). Assumes that up to 143 kkg from all categories goes to POTWs and 75% of this ends up in sewage sludge on land (U.S. EPA 1980).

[5] Law and Gordon (1979) give values for silver flow through a municipal incinerator processing 920 dry kkg solid waste per week. Total municipal solid waste (MSW) incinerated 10 kkg yr (U.S. EPA 1976). Smith and Carson (1977) suggest that combustible refuse may contain as much as 400 kkg silver annually.

[6] Assume 1 kg Ag atmospheric emission/920 kkg MSW and 10^7 kkg MSW/yr; yields 10 kkg Ag/yr.

[7] Assume 5 kg Ag in ash/920 kkg MSW and 10^7 kkg MSW/yr; yields 60 kkg Ag/ yr.

[8] Assume <0.3 kkgAg/yr.

[9] Estimate for discarded household appliances, appliances recycled into steel scrap and other non-combustible refuse (Smith and Carson 1977).

[10] The concentration of silver in the combustible fraction of MSW has been estimated at 3 mg/kg (Haynes et al. 1977). If this concentration is similar to that in the non-combustible fraction, and if 95% of MSW is not incinerated (10^7 out of 1.60×10^8 kkg MSW is incinerated), approximately 460 kkg of silver could go to landfills from non-combustible refuse. However, the 3 mg/kg assumption appears to be an unverified estimate. If instead, this is taken as a minimum concentration, since the non-combustible portion includes appliances, contacts, etc., which have a much higher silver content than combustibles, then 460 kkg also represents a minimum.

TABLE 15. SILVER MATERIALS BALANCE FOR POTWs AND REFUSE, 1978

Source	Input	Environmental Releases (kkg/yr)		
		Air	Land	Water
POTW	290[2]	neg[1]	220[2] (40)[3]	70[2]
	143[4]		107[4]	36[4]
Urban Refuse				
Incineration	70[5]	10[6]	60[7]	neg[8]
Landfill	310[9] 460[10]		310[9] 460[10]	

---

[1] Engineering judgment, Acurex Corp.

[2] Figures calculated from U.S. EPA data (see Table 12) based on 10^{11} l/day total POTW flow and median values for; influent Ag concentration = .008 mg/l; effluent Ag concentration = .002 mg/l. For land value, sludge is difference between influent and effluent loads and, therefore, includes recycled sludge. Effluent flow equals influent flow. Air emission assumed to be negligible.

[3] A second method of calculation based on 6 x 10^6 dry kkg sludge produced/yr (U.S. EPA 1979a), wet sludge ~95% water by weight, 0.368 mg/l Ag in wet sludge (see Table 12), and assume 1 liter wet sludge has same density as 1 liter of water (1 kg). Wet sludge flow rate = $\left(\frac{6 \times 10^6}{.05}\right)$ (1l/kg) (1 kg/10^3 kkg) = 1.1 x 10^{11} l/yr.

[4] Non-air discharge for photography (see Table 9). Assumes that up to 143 kkg from all categories goes to POTWs and 75% of this ends up in sewage sludge on land (U.S. EPA 1980).

[5] Law and Gordon (1979) give values for silver flow through a municipal incinerator processing 920 dry kkg solid waste per week. Total municipal solid waste (MSW) incinerated 10 kkg yr (U.S. EPA 1976). Smith and Carson (1977) suggest that combustible refuse may contain as much as 400 kkg silver annually.

[6] Assume 1 kg Ag atmospheric emission/920 kkg MSW and 10^7 kkg MSW/yr; yields 10 kkg Ag/yr.

[7] Assume 5 kg Ag in ash/920 kkg MSW and 10^7 kkg MSW/yr; yields 60 kkg Ag/ yr.

[8] Assume <0.3 kkgAg/yr.

[9] Estimate for discarded household appliances, appliances recycled into steel scrap and other non-combustible refuse (Smith and Carson 1977).

[10] The concentration of silver in the combustible fraction of MSW has been estimated at 3 mg/kg (Haynes et al. 1977). If this concentration is similar to that in the non-combustible fraction, and if 95% of MSW is not incinerated (10^7 out of 1.60 x 10^8 kkg MSW is incinerated), approximately 460 kkg of silver could go to landfills from non-combustible refuse. However, the 3 mg/kg assumption appears to be an unverified estimate. If instead, this is taken as a minimum concentration, since the non-combustible portion includes appliances, contacts, etc., which have a much higher silver content than combustibles, then 460 kkg also represents a minimum.

TABLE 16. SILVER DISTRIBUTION IN POTW SLUDGE; SELECTED U.S. CITIES

City City (Plant Location)	Average Flow (10 1/day)	Ag Concentration (ug/1) Influent	Effluent	Sludge (1°& 2° combined)	Range (ug/1)	No. Samples With Ag	Total Sampl
Indianapolis, IN	400	8	<2	107	2 - 18	18	23
Cincinnati, OH	30	1	ND	78	2 - 6	2	7
Lewiston, ME	38	1	<4	368	4 - 7	2	10
Atlanta, GA	340	18	3	1966	7 - 30	6	6
St. Louis, MO	95	23	2	1903	4 - 40	6	6
Pottstown, PA	23	15	3	1625	8 - 23	6	6
Grand Rapids, MI	190	5	1	117	2 - 11	5	6

Source: Unpublished data - U.S. EPA Effluent Guidelines Division; figures shown represent data fr
The study is ongoing and will be expanded to other urban centers.

It is further assumed that though silver is recycled within the activated sludge process, all of the metal will eventually be released. Although greater trace metal removal can be achieved with advanced treatment processes, less than 2% of the nation's POTWs use these advanced methods (Linstedt et al. 1971). On the basis of these assumptions, the discharges by POTWs are estimated to contain 220 kkg of silver in 1978.

An alternative method for estimating the annual silver discharge to sludge is to calculate silver release from the silver concentration in sludge and the quantity of dry sludge produced annually (5.5×10^6 kkg). If the silver concentration in POTW wet sludge is assumed to be 0.368 mg/l and wet sludge is assumed to be 95% water by weight, approximately 40 kkg are discharged to land.

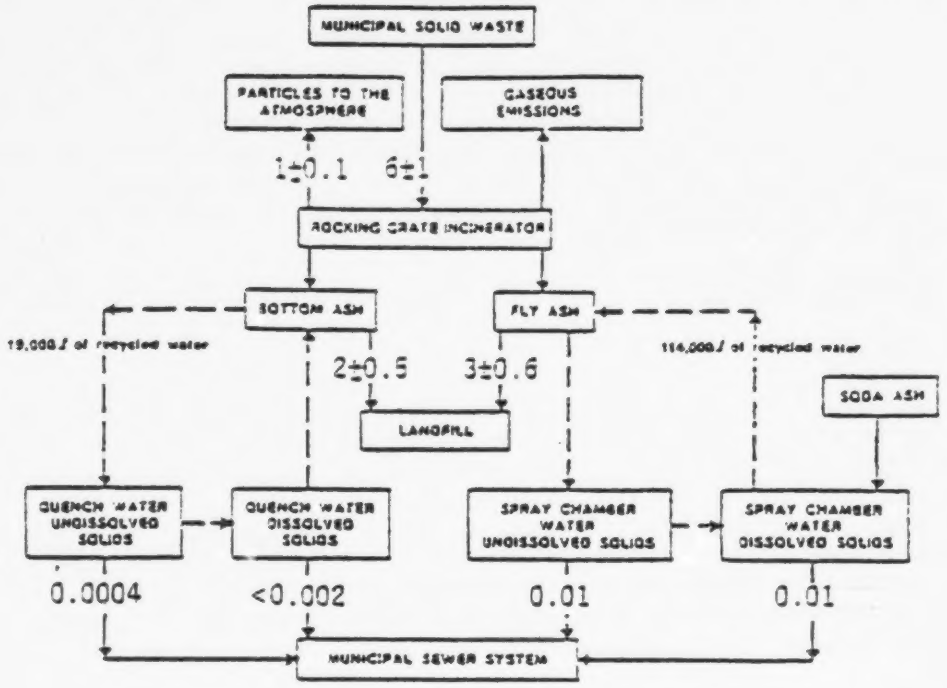
The U.S. EPA (U.S. EPA 1979a) has estimated the disposition of POTW sludge as follows:

landfill	24%
incineration	21%
ocean dumping	18%
food chain	15%
non-food chain	3%
giveaway/sale	11%
other (including stockpiling and storage in lagoons)	6%
unknown	2%

For this materials balance, silver releases to the environment in sludge are assumed to be releases to land because ocean dumping of sludge has been mandated to cease by 1981 and more stringent air quality standards may curb incineration of sludge (U.S. EPA 1979a).

2. Urban Refuse

The three options for handling of urban refuse are energy recovery (primarily by incineration), material recovery, and disposal through incineration or landfill. Urban refuse consists of two major components: the combustible fraction (paper, cardboard, plastics, fabrics, etc.) and the noncombustible fraction (ferrous and non-ferrous metals, glass, ceramics, etc.). Figure 6 depicts the flow of silver through a municipal incinerator processing 920 kkg of dry refuse per week (Law and Gordon 1979). From this material balance and an assumed annual volume of municipal solid waste totalling 10^7 kkg (U.S. EPA 1976a), silver loading to air and land is estimated to be 10 kkg and 60 kkg, respectively (Table 18). Water discharges from incineration processes are negligible. Law and Gordon (1979) postulate that non-combustibles are significant contributors to the total incinerator silver emissions, perhaps accounting for as much as two-thirds of the total, because not


MUNICIPAL SOLID WASTE
PARTICLES TO THE ATMOSPHERE
GASEOUS EMISSIONS
1±0.1
6±1
ROCKING GRATE INCINERATOR
BOTTOM ASH
FLY ASH
19,000 ℓ of recycled water
114,000 ℓ of recycled water
2±0.5
3±0.6
LANDFILL
SODA ASH
QUENCH WATER UNDISSOLVED SOLIDS
QUENCH WATER DISSOLVED SOLIDS
SPRAY CHAMBER WATER UNDISSOLVED SOLIDS
SPRAY CHAMBER WATER DISSOLVED SOLIDS
0.0004
<0.002
0.01
0.01
MUNICIPAL SEWER SYSTEM

Note: Based on input of 920 kkg of solid waste (combustibles and noncombustibles).
Numbers represent relative proportions.

Source: Law and Gordon (1979).

FIGURE 6 FLOW DIAGRAM OF SILVER IN A MUNICIPAL INCINERATOR

all of the incinerator output can be accounted for the silver content of the combustibles fraction.

Statistics concerning silver in landfill are difficult to obtain because of the myriad of possible contributors. Smith and Carson (1977) estimate that over 300 kkg of silver is disposed of on land in discarded home appliances, appliances recycled in steel scrap, and other non-combustibles, such as junked automobiles, lost jewelry, etc. Ten percent (by weight) of the approximately 1.6 x 10^8 kkg of municipal solid waste generated annually consists of metals, with 1% being non-ferrous metals (Gordon 1978). No information was available on what percentage of this amount of metal non-ferrous group is silver. (The behavior of silver in soil is discussed in Chapter IV, Pathway 2.)

G. NATURAL SOURCES

1. Overview

Natural background levels of silver are present in soil, water and air at very low concentrations. The original natural source is bedrock, both exposed and underlying soil, from which silver is released through the process of weathering. The following section discusses the natural distribution of silver in physical media and estimates the rate of deposition or release to surface water and air. All estimations should be used with caution due to the large degree of error associated with each number because of the use of average concentrations.

2. Silver-producing Ores

Silver occurs in rocks and soils, usually as a small component of sulfide minerals, as native silver, or in humus complexes. In natural waters, silver exists as Ag^+, colloidal complexes, or as a trace element in living organisms. Though widely distributed, elemental silver is typically present only in small amounts. Other sources of silver are silver-bearing minerals such as argentian tetrahedrite and tennantite, pyroustite, argentite, acanthite, pyragyrite, chloroargyrite, and argentojarosite (Smith and Carson 1977). The silver content of these and other common mineral forms is summarized in Table 17.

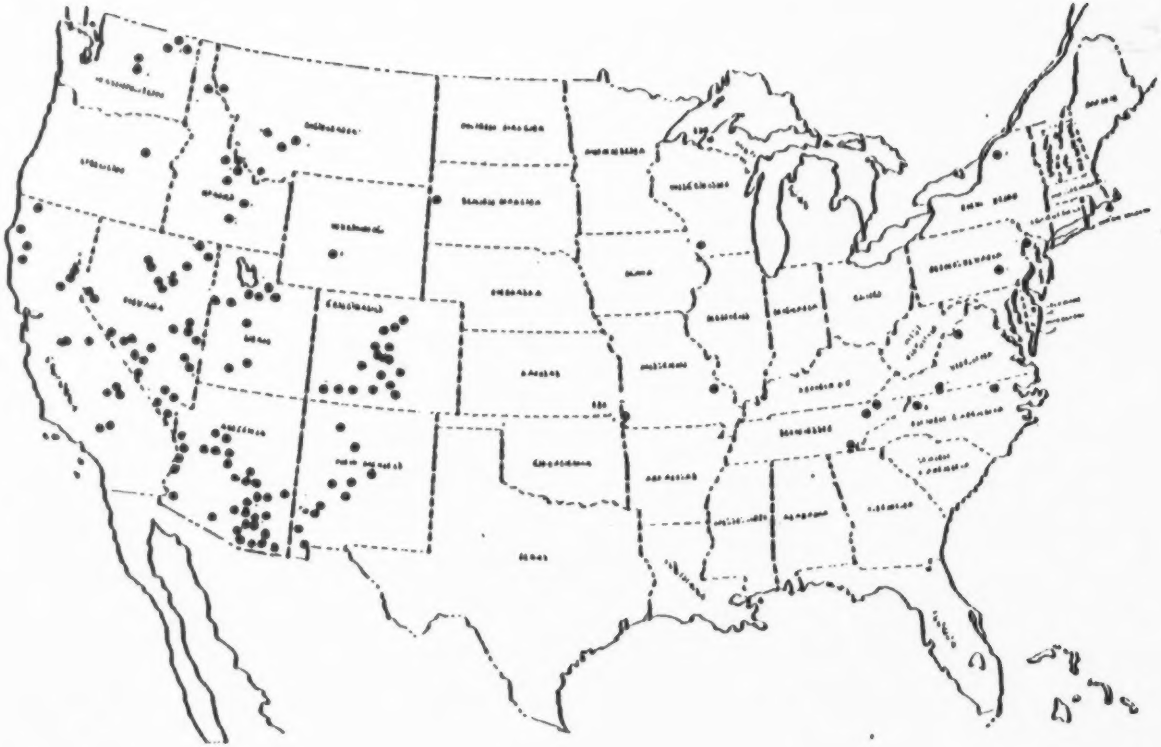
Silver deposits in the U.S. have been found mainly in Idaho, Nevada, Colorado, Arizona, Utah, New Mexico, and Michigan as shown in Figure 7. The silver content of individual deposits varies widely with geographic location. Argentian tetrahedrite in the Coeur d'Alene district of Idaho, for example, averages from 65 mg/kg to 335 mg/kg of silver but may contain 0.1 or more percent of silver; shale deposits in Michigan contain up to 150 mg/kg of silver; the silver content of sandstone is generally of the same range, but concentrations greater than 1000 mg/kg of silver (Silver Reef, Utah and in Michigan) are known (Smith and Carson 1977). Further discussion of natural levels in soil, air, water and biota and their comparison to anthropogenic levels can be found in Chapter IV-E.

TABLE 17. SILVER CONTENT OF SILVER ORES

Mineral Form	Chemical Formula	% Silver
Native Silver	Ag	100
Mineral Forms		
Argentiferous galena	AgPbs	
Argentite	αAg_2S	87
Acanthite	βAg_2S	
Argentian tetrahedrite	$(Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$	
Argentian tenanite		2.6 - 4.5
Pyroustite	$3Ag_2S.As_2S_3$	64.5 - 65.4
Pyrargyrite	$3Ag_2S.Sb_2S_3$	59.5 - 60.8
Chlorargyrite	AgCl	75.3
Argentojarosite	$Ag_2Fe_6(OH)_{12}(SO_4)_4$	
Stephanite	Ag_5SbS_4	68.3
Naumannite	Ag_2Se or $(Ag_2Pb)Se$	43.0
Hessite	Ag_2Te	63
Polybasite	$Ag_{16}Sb_2S_{11}$	75.6

Smith and Carson (1977)

Source: Smithells (1976) unless otherwise noted.



Source: Smith and Carson (1977).

FIGURE 7 GEOGRAPHIC DISTRIBUTION OF SILVER-PRODUCING ORES IN THE U.S.

3. Silver Releases in Aquatic Systems

Weathering of silver containing mineral deposits is reported to be responsible for the bulk of silver present in freshwater, 0.24 ug/l (Boyle 1968), with anthropogenic sources contributing only a small portion of the total load. Waters that leach silver-bearing natural deposits sometimes carry up to 100 times more silver than other fresh waters. Silver present in the suspended material in rivers and streams varies greatly; eastern rivers tend to carry higher silver concentrations than rivers west of the Mississippi, even though their suspended loads are lower (Smith and Carson 1977). Seawater, the ultimate reservoir for much of the continental sediment, has a silver concentration approximately the same as freshwater, ~0.2 ug/l.

Table 18 lists several pathways of silver to surface water and the estimated magnitude of each. Included are total U.S. runoff, urban runoff specifically, sediment release and precipitation. The numbers are based on average media concentrations and do not reflect the regional variability discussed in the previous section.

As mentioned earlier, silver enters surface water in runoff that picks up natural deposits of silver from soil and bedrock. In many circumstances, some releases from human activities will also be transported in runoff, e.g., from mine tailings, so that this contribution is not strictly of natural origin. The U.S. runoff number also includes urban runoff; however, the contribution from this pathway can be estimated separately.

Urban runoff receives silver from both natural and anthropogenic sources including background soil levels, contacts and conductors, brazing alloys and solders, and solid wastes disposed of in landfills. In eleven out of twelve samples of urban runoff water, silver was detected at concentrations of 3 to 8 ug/l (U.S. EPA 1977). Assuming an annual urban runoff volume of 2.1×10^{13} l (U.S. EPA 1977) then a release of 63 to 168 kkg of silver can be estimated. Combined sewers and separate storm sewers receive 57% of the total runoff, with the remaining 43% going to unsewered areas. Therefore up to 96 kkg and 72 kkg of silver go to sewers and surface water, respectively, according to the previous estimates.

The estimate of sediment loading assumes that sediment formed from weathering of stream beds, decay of organic material, and other sources contributes the silver present in the parent material to total concentrations in the water column.

Precipitation is a pathway leading to land, as well as surface water. A large fraction of silver in rain falls on land and is probably retained in the soil (Chapter IV) unless carried to water in runoff. The estimate has been included in Table 18 to give an idea of how it compares in magnitude to other pathways.

TABLE 18. ESTIMATED U.S. SILVER RELEASES TO SURFACE WATER FROM NATURAL SOURCES

Source	Silver Discharge (kkg/yr)	Comments
Freshwater Stream Supply	408	Based upon an overage U.S. annual runoff of 1.7 x 10^{15}1 (USGS 1978) and a silver concentration of 0.24 ug/1 (Boyle 1968).
Sediments	30	Estimate of mobilization of silver by weathering to sediment by Bertine and Goldberg (1971).
Urban Runoff	63 - 168	Based on annual U.S. urban runoff of 2.1 x 10^{13} 1 and silver concentration of 3 ug/1 to 8 ug/1 (U.S. EPA 1977).
Precipitation[a]	400	Based upon average U.S. annual precipitation of 2 x 10^{15}1 and silver concentration of 0.02 ug/1 (Rattonetti 1974).

[a] Note this number may include contribution from sources outside the U.S., e.g., ocean spray. See text.

4. Silver Releases in the Atmosphere

Silver is released to the atmosphere from a number of natural sources. Table 19 lists these sources, and when possible, their estimated annual contribution to the atmosphere. Due to the global rather than national pattern of atmospheric transport processes and the importance of the oceans as a source of aerosol, the atmospheric sources must be examined globally and not only within U.S. boundaries. The actual amount of silver entering the atmosphere over the United States annually cannot be estimated with the data available; therefore rates of atmospheric loading cannot be compared directly to those for runoff and sediment loadings by natural sources.

H. AREAS FOR FUTURE INVESTIGATION

All of the numbers derived for the silver materials balance are based on several assumptions, some of which have a great deal of uncertainty associated with them due to lack of data. Therefore, further study of these areas would improve the accuracy of the environmental materials balance for silver.

Recommendations for further study include a general survey of silver recovery techniques practiced by industries in light of recent increases in the market price of the metal, especially those of major aqueous dischargers such as the photography industry. Other information needs include: (1) a better estimate of the contribution of silver to the environment from natural sources, expecially in runoff; (2) identification of the sources of silver to POTWs (currently only 30% from industrial releases and an additional 33% from urban runoff can be accounted for); (3) integration of data concerning land disposal of used silver products and wastes with urban land disposal information (including product lifetimes or replacement rates) in order to prevent double counting; (4) quantification of discharges of silver from non-silver using electroplaters; and (5) information regarding the recovery practices of small professional photoprocessors, which do not have in-house facilities for treatment, in order to determine whether any discharge effluents directly to surface water.

I. SUMMARY

1. Anthropogenic Sources

a. Metals Production

Mining, milling and smelting of silver-containing ores and the smelting of new (bullion) and old scrap material containing silver, all release silver to the environment. It is not possible to keep a mass balance on the silver flow through mining, smelting and subsequent releases.

TABLE 19. ESTIMATED GLOBAL SILVER RELEASES TO THE ATMOSPHERE FROM NATURAL SOURCES

Source	Silver Discharge (kkg/yr)	Comments
Windblown dust (all sources)	50	Largest continental source from grinding and dispersion of soils and rocks. Estimate assumes a global dust production of 500 x 10^6 kkg/yr and silver concentration of 0.1 mg/kg (Boyle 1968).
Sea Salt Sprays	2	Not expected to be as important as for other metals (Mulvey 1979). Estimated based on global production of aerosols from se salt spray of 1000 x 10^6 kkg/yr (Elsaesser 1975) and silver concentration of 0.2 ug/l (Boyle 1968).
Volcanogenic particles	neg	No specific data available for silver; based on global aerosol production of 10 x 10^6 kkg/yr (Elsaesser 1975) and silver concentration of 0.1 mg/kg (Boyle 1968).
Forest fires	neg	Young and Jan (1977) estimate aerial fallouts of silver to a 10,000 km area to be 0.6 kkg/day and 0.15 kkg/day during and following a fire, respectively.
Meteoric debris	-	No specific data available for silver.

Approximately 1230 kkg of silver were mined in 1978, primarily in the form of silver ore and copper ore, with lesser quantities obtained from lead, gold, zinc and other ores. Primary and secondary smelting of ores and additional recycled scrap material extract a total 2840 kkg of silver annually.

An estimated 66 kkg silver are released to the environment from the processes of mining and milling, primarily during milling; 94% is released in solid form (tailings) to land, with less than 6% going to water and air. The locations of mines and mills processing silver are concentrated in Idaho, Colorado, Montana, Arizona, Utah and South Dakota.

From all smelting processes combined, a total of 134 kkg of silver is released to the environment, of which 77% goes to land in the form of slag, 3% to air in dust and fumes (from roasting and converting), and 20% to water, primarily in spent electrolyte solutions. The 27 smelters that process silver are scattered throughout the U. S.

b. Other Production Processes In Which Silver Is a Byproduct

Unintentional releases of silver occur during the processes of cement manufacturing, iron and steel production and coal and petroleum combustion. Of the 20 kkg of silver released by the three categories, 90% is released to water, 10% to soil, and a negligible amount to air. These releases are expected to be evenly distributed across the U.S., with generally higher rates of release in urban areas.

c. End Uses

The greatest consumer of silver is the photographic industry (40% of total production), followed by the manufacturers of contacts and conductors (~20%). Other consumers include electroplaters, jewelry-makers, producers of sterling ware, catalyst, brazing alloys and solders, batteries, coins, dental supplies, mirrors, bearings and cloud-seeding material.

Releases to the environment from consumers totalled approximately 1080 kkg in 1978 and reflected consumption patterns. The compartment receiving the largest amount of releases from consumers of silver was land (78%), followed by water (19% including POTW's). Air received only a minor fraction of the total releases (<3%). The biggest dischargers were the photographic industry and the contact/conductor industry, which together contributed 94% of consumer discharges, primarily to land. The brazing alloy/solder industry released 60 kkg of silver (7% of total releases to land). Most other industries had negligible silver discharges from both manufacture and use of silver-containing products.

The discharges from the photoprocessing industry included releases by producers of photographic equipment (films, solutions) and developers of film, both amateurs and professionals. Producers were responsible for approximately 50% of all photographic discharges to water. Thirty-eight percent of the total 142 kkg aqueous discharge was directed to surface water; the remainder to POTWs. Amateur photographers were estimated to discharge only 15 kkg to surface water or POTWs; professional developers were collectively estimated to discharge 50 kkg.

d. Municipal Disposal

Silver is released to POTWs and urban refuse landfills or incinerators during the ultimate disposal of silver in used products, sludge and effluents from wastewater treatment. An estimated 290 kkg of silver is discharged to POTWs of which 75% goes to land the remainder to surface water. An estimated 70 kkg of silver is incinerated, with approximately 86% going to solid waste and the remainder to air. Up to 460 kgg of silver is disposed of in landfills.

2. Natural Sources

Natural background levels of silver, as indicated by the location of silver-producing ores, are greatest in the western United States. The most significant natural pathways into the environment are in runoff to water (including urban runoff), in sediment formation, and in dust production. Transfer of silver from the atmosphere to soil and water takes place via precipitation. The total annual natural release of silver to U.S. surface water is estimated to be 438 kkg, of which up to 38% is urban runoff. The total amount of silver released to soil through surface and subsurface weathering of bedrock cannot be determined. There is a large amount of uncertainty associated with these estimates.

3. Conclusions

In conclusion, the greatest source of releases of silver to the environment from all sources (with a total of 710 kkg annually), appears to be release through natural weathering processes and transfer to other media (~69% of total). However, relative to natural sources, industrial production activities produce a significant mass of silver (~28%), some of which would be in a more mobile form (e.g., small particulates from smelters, vapors). Inadvertent releases of silver from certain cultural activities (e.g., fuel combustion) contribute a relatively minor fraction (~3%) of the total releases.

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CHAPTER IV.

ENVIRONMENTAL FATE AND DISTRIBUTION

A. INTRODUCTION

The purpose of this chapter is to ascertain the distribution and concentration of silver in different environmental compartments following release to the environment. Silver is not subject to many transformation processes under environmental conditions. It is subject primarily to transport processes, both in individual media and in intermedia movement between certain media. In addition, silver is released to the environment at low concentrations from a few, well-defined sources. Because there is an adequate data base describing both environmental levels and fate processes, the pathways approach was used to characterize the important processes determining the environmental fate of silver.

The following chapter is organized as follows:

B) Physical and Chemical Properties
C) Environmental Fate
D) Biological Fate
E) Concentrations Detected in the Environment
F) Summary and Conclusions

B. PHYSICAL AND CHEMICAL PROPERTIES

1. Physical Properties

Of the 27 known isotopes of silver, only ^{107}Ag and ^{109}Ag are found in nature and are not radioactive. They are present in roughly equal amounts, 51.82% and 48.18% of the total, respectively. Table 20 lists selected physical properties of silver.

In many respects, the physical properties of silver are different from other IB metals, copper, and gold. Metallic silver has the highest electrical and thermal conductivities of all the elements; silver has the lowest melting and boiling point of IB metals. The reflectivity of polished silver is also very high, although dependent on wave length; in the infrared region reflectivity approachs 98%, but falls to 10% at 3200°A.

2. Chemical Properties

Silver is a white, lustrous metal found in nature both in its elemental state and in association with various minerals, usually sulfides of copper, lead, and arsenic. It is the most reactive of the

TABLE 20. PHYSICAL PROPERTIES OF SILVER

Atomic weight	107.868
Melting point	960.8°C
Heat of fusion	2.855 kcal/g atom
Boiling point	2212°C
Heat of vaporization	60.72 kcal/g atom
Entropy of pure annealed silver at 298.15°K	10.20 e.u.
Entropy of transition, solid-liquid	2.313 e.u.
Entropy of transition, liquid-gas	24.43 e.u.
Heat of sublimation	68.14 ± 0.2 kcal/g mole
Vapour pressure of liquid silver, mm Hg	temp. °C
10^{-1}	1190
1	1360
10	1580
100	1870
760	2212
Vapour pressure of solid silver, 735-960°C	
$\log P_{mmHg} = \frac{-1.4580\times10^{4}+9.22}{T(^\circ Abs)}$	
Vapour pressure of liquid silver .965-2152°C	
$\log P_{atm} = \frac{-1.3680\times10^{4}+5.615}{T(^\circ Abs)}$	
Critical temperature	4394°C
Critical pressure	336 atm
Critical volume	339 cc/g mole
Density of solid silver (depends on sample and sample history)	10.491 g/cc (metal cast then fully annealed)
Density of liquid silver (over whole normal liquid range)	10.465-0.0009067 T g/cc
Coefficient of expansion (0-100°C)	19.10×10^{-6}
Coefficient of expansion 90°A	14.06×10^{-6}
Specific heat (0-800°C)C,= $0.055401+0.14414\times10^{-4}T-0.16216\times10^{-3}T^2$	cal/g/°C
Specific heat of liquid silver up to 1300°C	0.0692 cal/g/°C
Specific heat of silver vapour	~0.046 cal/g/°C
Thermal conductivity (at 0°C)	0.999 cal/sec/cm^2/°C/cm
Electrical conductivity (20°C)	1.59 µΩ cm
Temperature coefficient of conductivity (20°C)	3.93×10^{-3} per °C
Ionization potentials:	
1st: 7.574 cV	
2nd: 21.48 cV	
3rd: 34.82 cV	
Crystal structure Face-centered cubic	Lattice constant a=4.086Å
Ag=Ag bond length (15°C)	2.8894Å
Ag-Ag bond strength	28.5 kcal/mole

TABLE 20. PHYSICAL PROPERTIES OF SILVER (continued)

Crystal ionic radius	Ag^{+}	= 1.26 Å
	Ag^{++}	= 0.89 Å
Viscosity	1000°C	3.89 cp
	1100°C	3.89 cp
Surface tension (1268°K)		920 dynes/cm
Magnetic susceptibility		$-0.181x10^{-6}$ cgs units/g

Source: Thompson (1973).

noble metals and dissolves in oxidizing acid and in cyanide solutions in the presence of oxygen or peroxide; although silver is not oxidized at room temperature by oxygen, a thin oxide film forms at 200°C. The most common oxidation state is +1, and although Ag(II) and Ag(III) are known, they are unstable in the aqueous environment. A descriptive review of the chemistry of silver has been given by Thompson (1973).

The chemistry of silver also bears few resemblances to copper and gold. Comparisons between silver and alkali metals, which also have a single s electron, are not useful. A better analogy, in terms of chemical behavior and reactivity, would be to palladium, from which silver differs electronically only by its possession of a 5s electron. Although the Ag(I) is the most common oxidation state, Ag(II) and Ag(III) are known and may be of importance in catalytic oxidation processes (Cotton and Wilkinson 1973). The importance of Ag(II) and Ag(III) in the environment is unknown.

Numerous silver compounds are photosensitive, the most important of which are (in order of sensitivity) silver, bromide, and chloride. Other photosensitive compounds are silver(I) fluoride, iodide, oxide, imide, phosphate, sulphite, and dithionate. This phenomenon is, in fact, the basis of the photographic industry (silver salts are not, however, used solely because of their photsensitivity). Upon irradiation at wavelengths less than 400 nm, silver halides are reduced to elemental silver and halogen.

$$\mathrm{Ag\,X} \longrightarrow \mathrm{Ag}^{\circ} + \mathrm{X}^{\circ}$$

Once a silver atom has been formed, according to the Gurney-Mott mechanism, a silver atomic center can trap an electron and then a second mobile silver ion, thus forming a more stable silver center, Ag_2 (Pouradier et al. 1977). This aggregation can continue as long as light is supplied. This effect is not restricted to halides, but is general for other photosensitive silver compounds.

A wide variety of silver(I) compounds are known, including organosilver compounds as well as the more typical inorganic compounds and complexes. Compounds commonly found in nature or which are often released to the environment include: bromide, chloride, fluoride, iodide, cyanide, thiocyanate, oxide, hydroxide, sulphide, carbonate, nitrate, sulphate, as well as Ag(I) complexes with ferrocyanide and thiosulfate. The majority of these compounds are relatively insoluble (see Table 21). Silver nitrate is the most notable exception.

With regard to environmental transport, silver complexes involving halides, cyanides, amines, and thiosulfates are particularly important. Stability constants for various complexes are shown in Table 22. In natural systems where more than one ligand type is present, mixed complexes exist in equilibrium with homogeneous complexes. A variety of mixed silver complexes are listed in Table 23. Polynuclear silver complexes may also be important. For example, argentothiosulfate complexes are formed in exhausted photographic fixing booths.

TABLE 21. SOLUBILITY PRODUCTS OF VARIOUS SILVER SALTS

	$(-\log S)$[1]	
Salt	$\mu=0$	$\mu=.1$
A_gOH	7.71	7.6
Ag_2CrO_4	11.95	11.3
$Ag_2Cr_2O_7$	6.7, dil.[2]	
Ag_2MoO_4	11.55	10.9
Ag_2WO_4	11.26	10.6
$Ag_4[Fe(CN)_6]$	40.8,dil.[2]	
$Ag[Ag(CN)_2]$		11.3, var.[3]
AgCNO	6.64	6.5
AgSCN	11.97	11.7
Ag_2CO_3	11.09	10.4
AgN_3	8.54	8.3
Ag_3PO_4	15.84	14.7
Ag_3AsO_4	19.95	18.9
Ag_2S	49.2	48.2
Ag_2SO	4.80	4.1
AgCl	9.752	9.50
AgBr	12.305	12.06
$AgBrO_3$	4.28	4.0
AgI	16.08	15.83
$AgIO_3$	7.51	7.3
$Ag_2C_2O_4$	11.0	10.4
A_gCH_3COOH	2.7	2.1

---

1. Most values refer to a temperature of 20 or 25°C.
2. Dilute solution, below 0.01M
3. Ionic strength was not specified.

Source: Ringbom (1963).

TABLE 22. DISSOCIATION OF HOMOGENEOUS SILVER COMPLEXES IN WATER AT ROOM TEMPERATURE

Ligand	Stability Constant				
	pK^1_{sp}	pK_1	pK_2	pK_3	pK_4
Cl	9.75	3.3	5.25	5.7	5.4
Br	12.31	4.5	7.4	8.5	9.0
I	16.09	7.5	11.6	14	15
CN	15.8	9	20.7	21.9	21
SCN	11.97	4-5	8	10.3	10.9
SeCN	15.4	--	11.0	13.8	
SO	13.8	5.5	8.7	8.9	
SO	4.9				
S O		9	13.3	13.9	
Thiourea		7.3	10.6	12.8	13.7
S	49.1				
HS		13.2	17.2		
Se	63.7				
OH	7.71	2.0	4.0		
NH		3.3	7.2		
Aliphatic primary amines		3.0-3.5	6.8-7.5		
Aliphatic secondary amines		3	5.3-6.4		
Aliphatic tertiary amines		2.6	3.6-4.6		
Diethylenetriamine		6.1			
1-Ethylenediamine		5.0	7.8		
1,2,3-Triaminopropane		5.6			
Triaminotriethylamine		7.8			
Triethylenetetramine		7.7			
Ethylenediaminetetraacetate (EDTA)		7.0			
Piperidine		3.0	6.5		
Pyridine		2.0	4.2		
Imidazole		3.5	6.9		
Ethanolamine		3.2	6.8		
Triethanolamine		2.3	4		

TABLE 22. DISSOCIATION OF HOMOGENEOUS SILVER COMPLEXES IN WATER AT ROOM TEMPERATURE (Continued)

Ligand	Stability Constant				
	pK_{sp}	pK_1	pK_2	pK_3	pK_4
a-Amino acids without complexing residue on the side chain		3.5–3.7	7.0–7.2		
Arginine		3.5	8		
Cysteine		5.2	18.2		
Histidine (neutral medium)		--	7.5		
(high pH)		7.3	8.9		
Methionine (low pH)		3.2	5.7		
w-1-3 to 1-6-n-Amino acids		3.4–3.7	7.5–7.8		
Monothioglycol	19.6	13.2	17.8		
Thiosemicarbazide				12.8	
1-Phenyl-5-mercaptotetrazole	16.2	10.9	13.6	15.3	

Source: Pouvradier _et al_. (1977).

TABLE 23. DISSOCIATION CONSTANTS OF MIXED SILVER COMPLEXES IN WATER AT ROOM TEMPERATURE

Ligands		Total No. Tied Ligands					
		2	3				4
L^{I}	L^{II}	pk	pk	.pk	pk	pk	pk
Cl	Br				9.5		7.9
Cl	I			7.6			
Br	I		13.5	12.3	13.8		
I	SCN	12.1					
I	SeCN		15.4		14.7		14.7
SCN	SeCN			13.8	13.4		
Cl	OH	4.7					
CN	OH	13.2					
Cl	SO		7.8	7.1			
I	SO	9.2	10.2	12.5			
CN	SO		11.1			14.4	
Cl	S O		10.8				
Br	S O		12.0	11.3			10.0
I	S O		13.2	13.6			13.5
CN	S O		15.7			18.1	21.3
Cl	NH	6.3	7.1				
Br	NH		7.6			7.8	
Cl	thiourea				12.6		
Br	thiourea				13.1		
I	thiourea		13.9			14.5	14.2
CN	thiourea				15.5	18.8	

Source: Pouvradier et al. (1977).

C. ENVIRONMENTAL FATE

1. Methodology

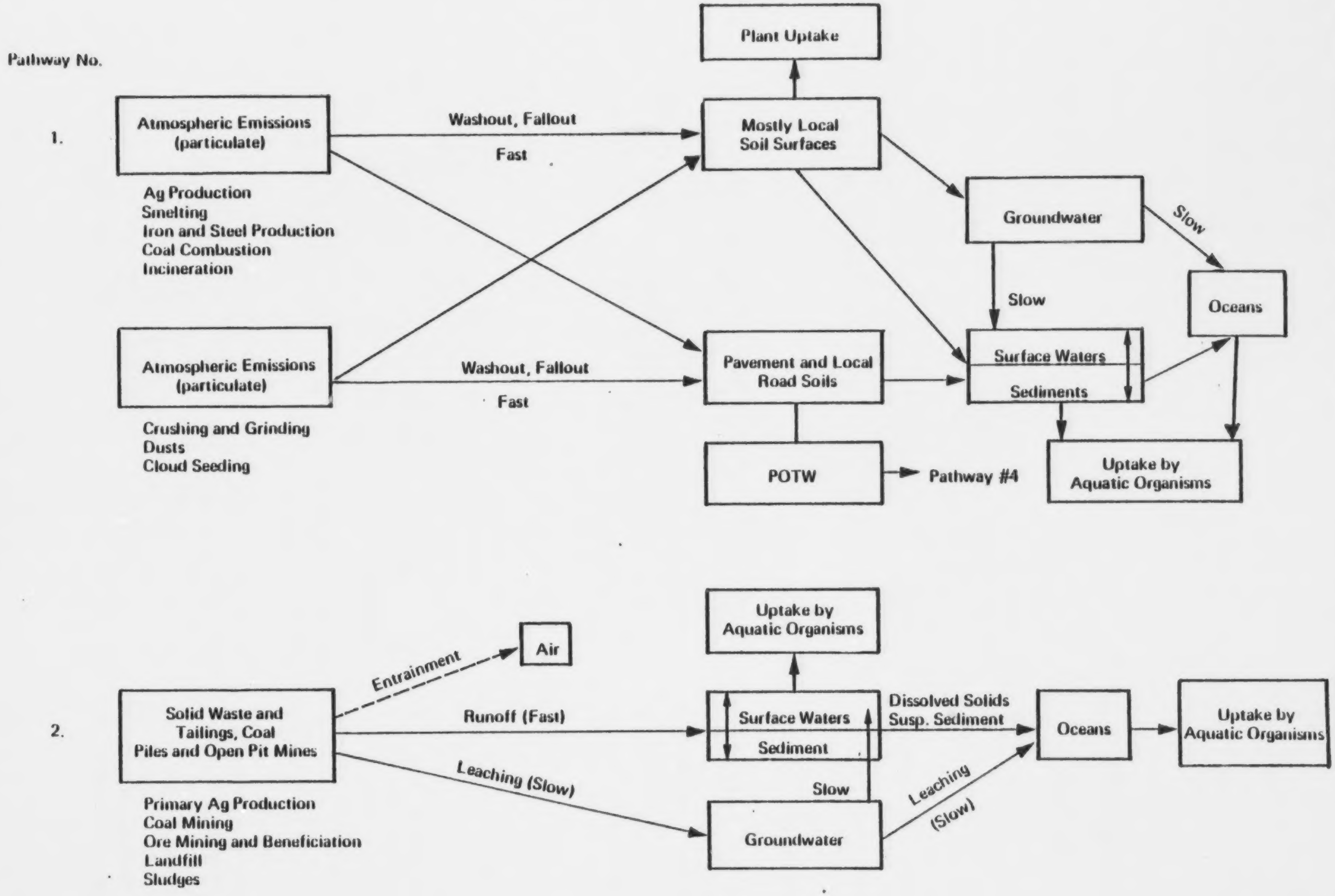
This section characterizes the physiochemical and bulk transport processes that determine the fate of silver released to air, water, and soil. Pathways are described for the major sources of environmental releases. A general overview of the environmental chemistry of silver conducted by Versar, Inc. (1979) has been used as the basis for judgments concerning the directions and rate of transport silver in an ecosystem. Additional studies available in the literature are cited as necessary. Biological pathways are treated separately in Section D. of this chapter.

2. Major Environmental Pathways

The major pathways of physical transport and the qualitative rates at which they occur are designated in Figure 8. Atmospheric emissions (Pathway 1) have been separated into point source and dispersive emissions. Combustion processes--such as incineration and smelting/refining--and the processes of brazing alloys, soldering and photoprocessing contribute to localized pollution. Releases from cloud seeding, mining and milling are more widely dispersed and contribute to the concentrations of silver found in urban runoff.

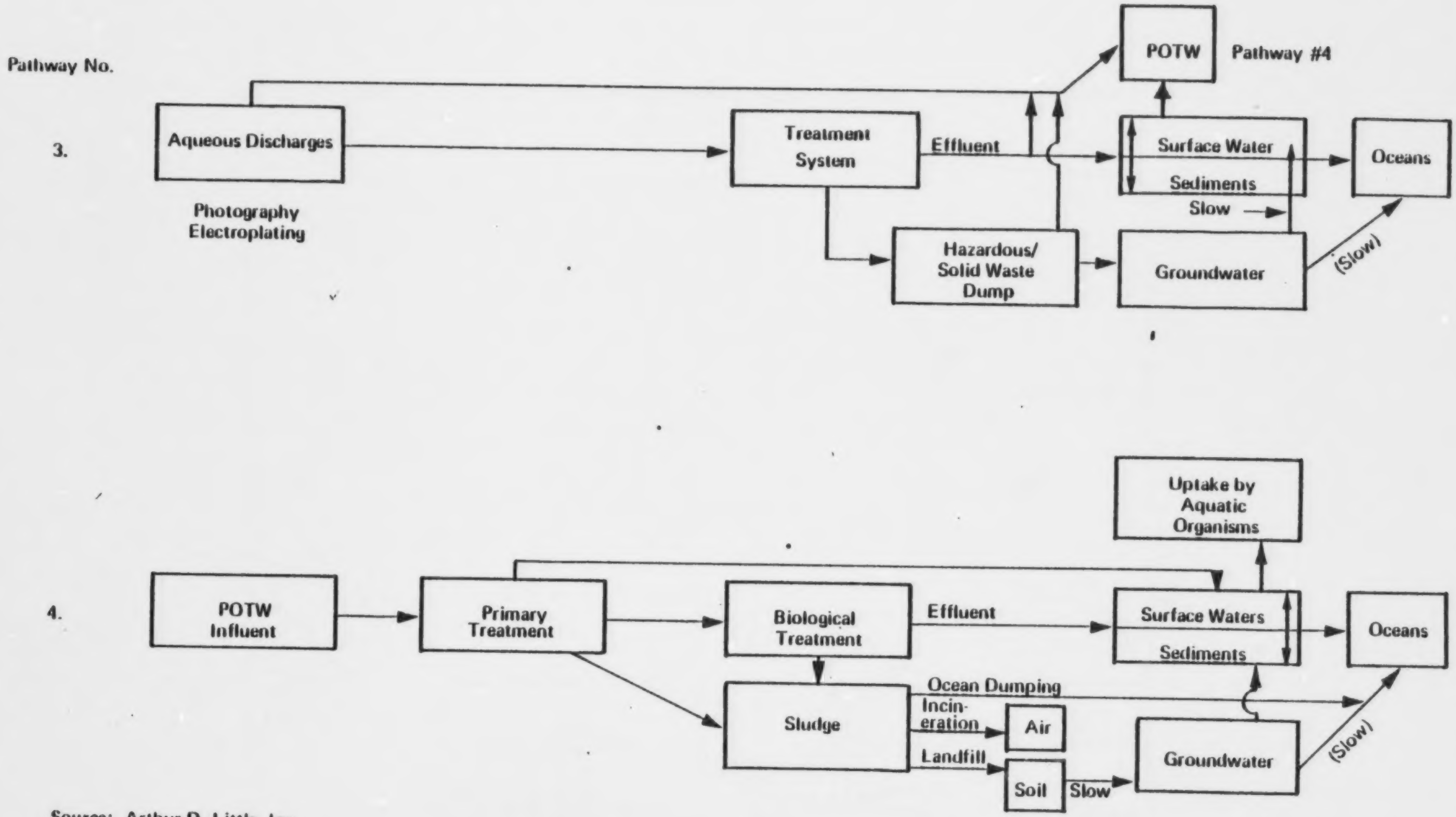
Pathway 2 in Figure 8 follows the flow of silver that originates from solid waste disposal sites and mine tailings. The industrial processes that contribute the largest amounts of solid waste (in the form of sludge or solid material) include photoprocessing, contacts/conductors production, smelting and refining, and brazing alloys and solders production. As environmental controls restrain further discharges to air and water, the quantity of silver disposed upon land surfaces can be expected to increase. The fate of silver discharged with process effluents by industries such as electroplating and photography into local surface waters or publicly-owned treatment works (POTW) is reviewed in Pathway 3. The fate of silver in influent to POTW's is described in Pathway 4.

Figure 9 gives an overview of all of the major pathways of anthropogenic silver in the environment. The land compartment receives a substantial portion of all silver releases. The migration of ground waters containing silver to nearby surface waters has not been shown in this figure since (1) the process is very slow, and (2) the current magnitude of this transport pathway has not been well documented. Also the silver in sediments is not represented, nor is the silver in soils resulting from atmospheric fallout.


Pathway No.
1.
Atmospheric Emissions (particulate)
Ag Production
Smelting
Iron and Steel Production
Coal Combustion
Incineration
Atmospheric Emissions (particulate)
Crushing and Grinding
Dusts
Cloud Seeding
Washout, Fallout
Fast
Washout, Fallout
Fast
Plant Uptake
Mostly Local Soil Surfaces
Pavement and Local Road Soils
POTW
Pathway #4
Groundwater
Slow
Slow
Oceans
Surface Waters
Sediments
Uptake by Aquatic Organisms
2.
Solid Waste and Tailings, Coal Piles and Open Pit Mines
Primary Ag Production
Coal Mining
Ore Mining and Beneficiation
Landfill
Sludges
Entrainment
Air
Runoff (Fast)
Leaching (Slow)
Uptake by Aquatic Organisms
Surface Waters
Sediment
Slow
Groundwater
Dissolved Solids
Susp. Sediment
Leaching
(Slow)
Oceans
Uptake by Aquatic Organisms

Source: Arthur D. Little, Inc.

FIGURE 8 MAJOR ENVIRONMENTAL PATHWAYS OF SILVER RELEASES


Pathway No.
3.
Aqueous Discharges
Photography
Electroplating
Treatment System
Effluent
Hazardous/ Solid Waste Dump
POTW
Pathway #4
Surface Water
Sediments
Slow
Groundwater
(Slow)
Oceans
4.
POTW Influent
Primary Treatment
Biological Treatment
Effluent
Sludge
Ocean Dumping
Incin-eration
Air
Landfill
Soil
Slow
Groundwater
(Slow)
Uptake by Aquatic Organisms
Surface Waters
Sediments
Oceans

Source: Arthur D. Little, Inc.

FIGURE 8 MAJOR ENVIRONMENTAL PATHWAYS OF SILVER RELEASES (continued)

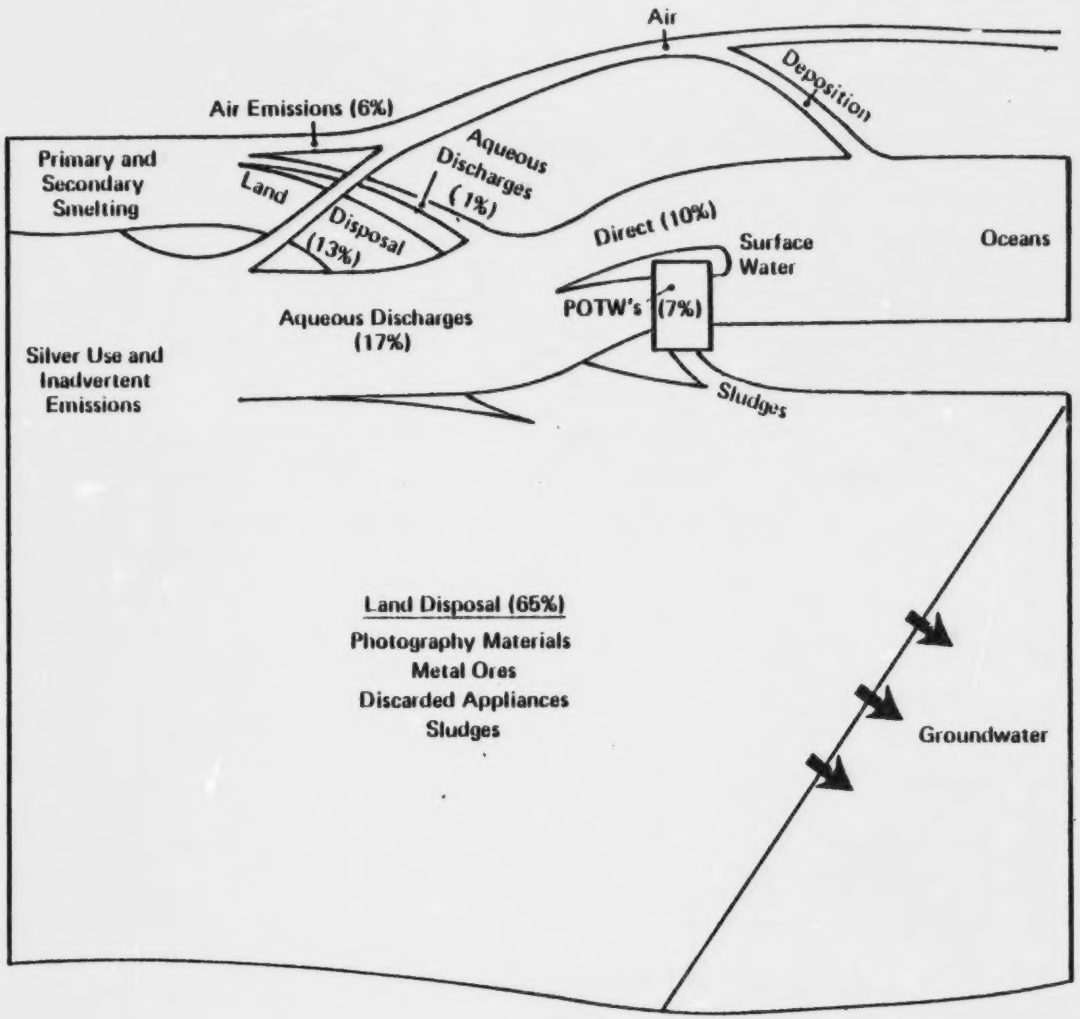

Air
Deposition
Air Emissions (6%)
Primary and Secondary Smelting
Aqueous Discharges (1%)
Land Disposal (13%)
Direct (10%)
Surface Water
Oceans
POTW's (7%)
Aqueous Discharges (17%)
Silver Use and Inadvertent Emissions
Sludges
Land Disposal (65%)
Photography Materials
Metal Ores
Discarded Appliances
Sludges
Groundwater

FIGURE 9 MAJOR PATHWAYS OF ANTHROPOGENIC SILVER RELEASED TO THE ENVIRONMENT

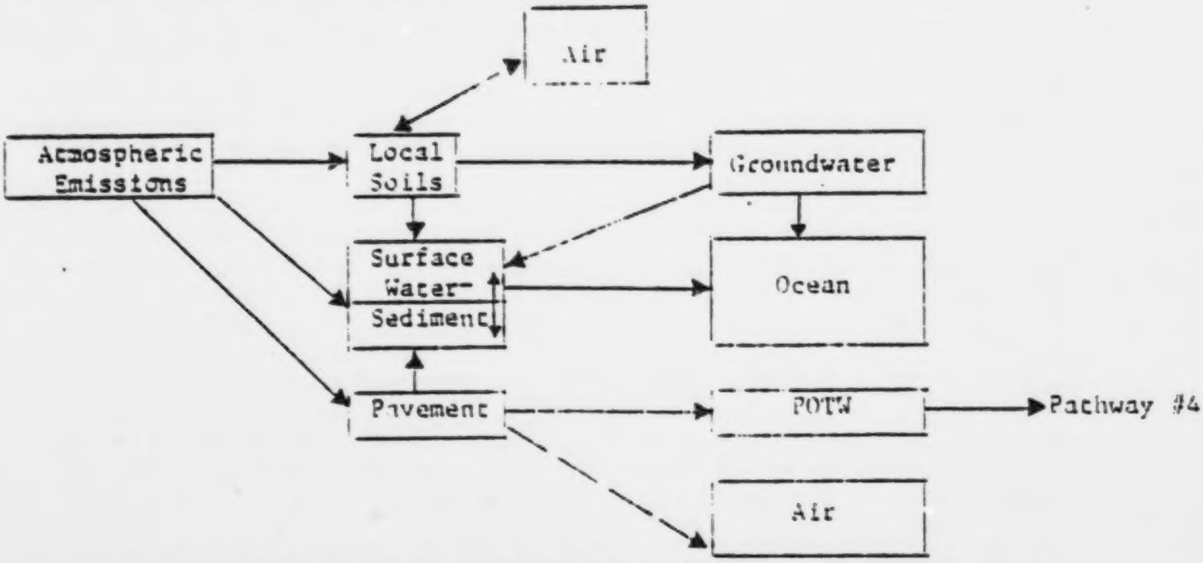
3. Important Fate Processes

a. Overview

Silver is released into the atmosphere from stacks and flues both from industrial processes and from inadvertent sources such as coal combustion. Particle size, height or release, and chemical speciation determine the residence time of silver in the atmosphere although little is known about the specific influence of these parameters. Generally large particulates generated from mining operations, such as grinding, settle in the vicinity of the source; smaller particulates from smelters are airborne for a longer period and eventually deposited with rainfall.

Silver deposited onto soils by atmospheric fallout, agricultural use, and solid waste disposal is largely in the form of insoluble compounds or is quickly sorbed onto clays or organic matter and thus becomes insoluble. Silver is so strongly adsorbed in soils that leaching of silver is not a probable transport route. High concentrations of silver on soil surfaces will be reduced by erosion and soil runoff. In waters, silver will be concentrated in the sediments, associated with clays and organic matter, or as a precipitated species, such as AgCl or Ag_2S.

b. Pathway 1 - Atmospheric Transport



Physical and Chemical Characteristics: The fate of silver in the atmosphere is expected to depend upon particle size, the chemical form, and the height at which the release occurs. Unfortunately, very little is known regarding the distribution of particle sizes of airborne silver or its chemical forms. Consequently, most of the literature describing the environmental fate of atmospheric silver relies on inference from the observed distribution of other metals that are also likely to be present concurrently with silver emissions.

Silver may be released as a fume or an aerosol. The metal's low melting point and vapor pressure insure that fumes are rapdily converted to fine particulates, much less than 20 um in aerodynamic diameter. Particles of this size will typically remain airborne for large distances from the source, and are more likely to be rained out than to settle out. Particles released by mechanical abrasion, as in ore crushing and grinding, are likely to be much larger >20 um) and will tend to be deposited by settling within a kilometer or so of the source.

The chemical forms of atmospheric silver are essentially unknown. Though most thermodynamically plausible species are relatively insoluble in water, Smith and Carson (1977) speculate that mining and milling operations will release silver to the atmosphere in the same chemical forms as are present in the ores--predominantly sulfides, chlorides, or sulfates. Releases from smelting, coal combustion, and iron and steel making are from combustion zones; since these have a high sulfur concentration, silver releases are likely to consist of sulfides, sulfates, and oxides. Silver oxides may be readily converted to carbonates in the atmosphere. Other combustion sources that emit silver, such as cement kilns and solder usage, are likely to release silver or silver oxides.

Crushing, grinding, sorting, etc. of ores containing silver and coal generate relatively course particulates. Since these processes seldom lead to emissions from an elevated stack, the impacts of such sources are likely to be localized (within about a kilometer of the source). Most of the total emissions from such sources will be deposited locally by gravitational settling. During precipitation, these large particles will be effectively scavenged by rainfall and deposited on land.

Fine particulates that pass particulate control devices (such as cyclones, electrostatic precipitators, and baghouses) at ore smelters, fossil-fuel fired power plants, and solid waste incinerators are generally smaller than 5 um in aerodynamic diameter. When released from tall stacks, these particulates will be dispersed widely, as indicated in the study by Klein and Russell (1973) of a coal-fired power plant on Lake Michigan. Silver contamination was observed over an area of 115 square miles and accounted for 80% of the silver emitted by the plant over its lifetime. The degree of silver contamination observed in this study was not severe: contaminated soils averaging only 0.272 mg/kg, compared with a background level of 0.247 mg/kg.

At a smelter in Idaho, Ragaini et al. (1977) found much higher concentrations of silver, averaging 20.0 ± 10.2 mg/kg compared with a background of 3.3 mg/kg. Rugged topography at that site constrained wind patterns such that Ag contamination was confined to the river valley. Nonetheless, elevated levels of silver were observed about 4 miles from the smelter complex. In the soil profile, levels of silver in contaminated soils fell rapidly with depth from the surface to a 20-cm depth, indicating the metal's immobilization in soil.

The data of Ananth et al. (1976) show that several metals with relatively high vapor pressures (Cd, Mn, Pb, and Cr) all occur at significant concentrations in the finer size particulate fractions of coal fly ash (1.5 um) as compared with coarse fractions (up to 25 um). Concentrations of these metals in the fine partiuclates range from a factor of 1.7 to 20 times greater than in the coarse fractions (median ratio is 2.4). Metals having lower vapor pressures (Al, B, Be, Cu, Fe, Ni, and V) did not exhibit this preference for the finer particulate size fractions, with a median ratio of concentrations between fine (1.5 um) and coarse (25 um) fractions of 1, and a range of 0.8 to 1.7. The high vapor pressure of Ag places it in the former group, and it is inferred that Ag will be concentrated preferentially in the finer fly ash particulates, which are more likely to pass through particulate control devices and are dispersed over wide areas.

Major Point Sources: The association between silver contamination of the atmosphere or soil and a major point source has been demonstrated clearly only for the above-mentioned power plants and smelter complex. Although some investigators have identified iron and steel mills as a major source of airborne silver, ambient monitoring data reviewed by Smith and Carson (1977) for the vicinity of three steel mills did not indicate a significant variation in ambient levels associated with the mills. The monitoring data were for a highly industrialized area, in which background levels of silver were comparatively high.

Galloway and Likens (1977) analyzed sediment core samples from a remote Adirondack lake for silver and found much higher concentrations in near-surface sediments than in deeper sediments. They conclude that the profiles reflect recent increases in the rate of silver deposition from the atmosphere.

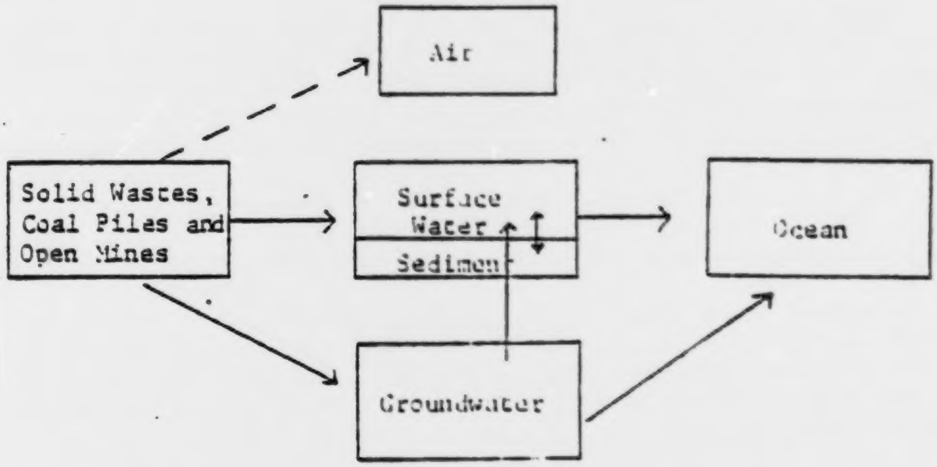
The use of silver iodide in weather modification, particularly for enhancement of winter precipitation in the Colorado River Basin, has been shown to have relatively little ecological effect by Cooper and Jolly (1970). Freeman (1977) presents extensive multi-media data for a Colorado alpine lake/watershed showing relatively little enrichment of silver in this watershed within the target area for silver iodide cloud-seeding experiments.

Summary Statement: Silver released during smelting and from inadvertent sources such as incinerators and coal combustion plants is likely to be associated with the particulates less than 20 um in diameter. This will permit wide dispersal of silver, with rainout as the primary mechanism leading to silver deposition onto land or surface waters. Of the silver released during smelting, coal combustion, photoprocessing and other industrial processing, roughly one-half of the silver will be dispersed more than 100 km from its source and eventually deposited by rain. The speciation of silver is not really known, but it is suspected that silver will exist predominantly as sulfides, chlorides, and sulfates in the ore.

Mechanical operations, such as grinding and crushing lead, to emissions of silver in larger particulates. These are expected to be short lived in the atmosphere and to be deposited within a kilometer of the source.

No enrichment of otherwise virgin lakes has been noted from use of silver iodide for cloud-seeding purposes. The amount of silver used in this capacity is expected to decrease due to increasing costs of the precious metal and replacement by other substances in cloud-seeding applications.

c. Pathway 2 - Land Disposal



Forms of Silver in Soil: Lindsay and Sadiq (1979) have recently reviewed the theoretical relationships of silver in soils. Oxides, sulfates, carbonates, and phosphates of silver are too soluble to persist in soils. Silver bromide, chloride, and iodide are the likely forms of silver in soil; under reduced conditions Ag° is formed. Complexes with halides (and possibly NH_3) may be important in soil systems. Under reducing conditions, AgHS becomes a significant silver complex. Under typical soil conditions, therefore, only a minor fraction of silver is expected to be present as free ionic silver.

Sources: The land is the major recipient of silver releases to the environment. Sources to land include tailing piles from metal ore and coal mining; landfills of municipal solid wastes, photographic wastes, incinerator fly ash, and sludges; and incorporation of wastewater effluents and sludges for agricultural purposes. These three categories are discussed individually.

Tailings and Mining Wastes: Silver is refined directly from silver ores or as a byproduct of copper, zinc, gold, and lead ores. Approximately 50% of silver is a product of base-metal ores. The remaining 50% is obtained from "silver ores" (Chapter III). Silver concentrations in coal range from 0.02-0.04 mg/kg up to 300 mg/kg and from approximately 0.001 mg/kg up to 100 mg/kg in crude oil (Chapter II, Smith and Carson 1977). The form of silver in these energy sources is a metal-organic complex. Some also occurs in the pyrite found in coal (Smith and Carson, 1977).

The major loss of silver due to milling and refining occurs in the flotation effluent (Smith and Carson 1977). This effluent is discharged to tailing ponds when recommended disposal practices are observed. In the past (as late as 1968) direct discharge to surface waters was practiced. Leonard (1977) found that negligible solid waste disposal results from silver production at smelters designed for lead, zinc, and copper refining. Any solid residue generated from silver refining is recycled in order to ensure the maximum recovery of silver.

Tailing ponds are made either by depositing tailings behind earth dams or by building the dams from tailings (Smith and Carson 1977). Some tailing leachate is trapped in order to recover any precious metals. Silver is recovered as Ag_2S by a precipitation technique. Activated carbon and electro-oxidation are other methods used to recover silver from tailings leachate.

Metal concentrations in leachate resulting from abandoned mine tailings has been studied extensively in the Coeur d'Alene mining area of Idaho. Until 1968, concentrator tailings were discharged directly into the Coeur d'Alene River, although leaching of the tailings waste has not been demonstrated to increase silver levels in the river (Smith and Carson 1977).

Galbraith et al. (1972) analyzed the trace metal concentrations in ground water underneath abandoned mine tailings in Cataldo Mission Flats of the Coeur d'Alene mining district. The concentration of silver in the tailings was 12.5 mg/kg at a depth of 3 feet, and about 0.5 mg/kg at 6 feet. The concentration of silver dissolved from the tailings was "too low to measure accurately" but ranged between 0.01 mg/kg and0.02 mg/kg. For metals in general, the authors hypothesized that sulfur-oxidizing bacteria cause formation of H_2SO_4 from sulfide, resulting in pH reduction and dissolution of the metals. At a pH of 6.6, sulfur-reducing bacteria precipitate the metals as sulfides. Since the pH decreases with depth in the tailings (killing off the sulfur-reducing bacteria), more dissolution occurs deeper in the tailings. The applicability of this theory to silver is borderline, since silver solubility, unlike that of most metals, increases as pH increases.

Trace metal distribution in groundwater of a mineralized region in Colorado was analyzed in order to determine if the mineralized area contributed to drinking water contamination (Klusman and Edwards, 1976). Silver was found in concentrations ranging from 0.5 ug/l to 5 ug/l in samples collected from wells. The results obtained do not illustrate any clear trend with regard to silver concentrations resulting from mineralization.

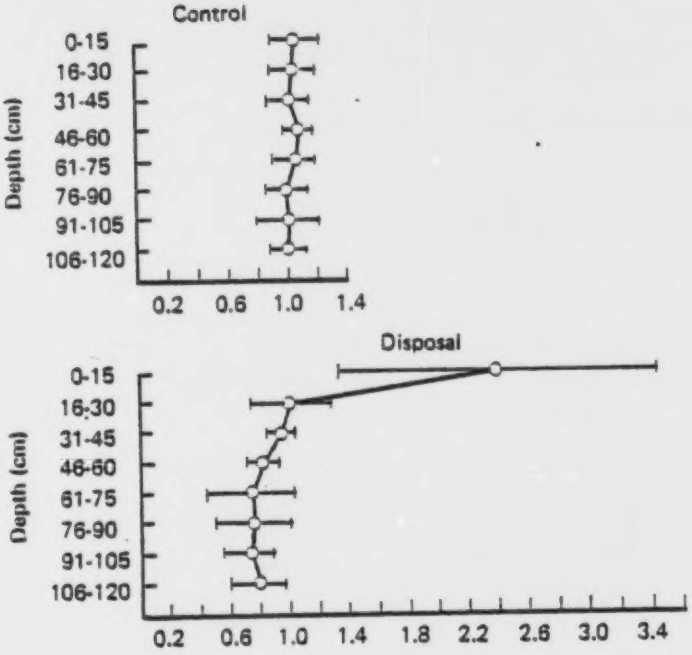
Wachter (1977) analyzed heavy metal concentrations in leachate originating from coal piles stocked for production and use purposes. Eight samples were subjected to a simulated rain equivalent to an average yearly rainfall. Silver concentrations were below the detection limit for all samples. (The detection limit was not specified.)

Acid Mine Drainage: Silver is apparently not a problem metal in acid mine drainage. Smith and Carson (1977) reported that the concentration of silver in acid mine drainage ranges from 1 ug/l to 8 ug/l, which is significantly lower than the concentrations of other metals.

Landfills: Little information was available concerning silver leaching from municipal or hazardous waste landfills to the ground water. Smith and Carson report that silver is quite inert as a constituent of solid waste, and, although its form in sludge is not well known, it is considered fairly resistant to mobilization. Law (1978) studied the metal constituents in municipal and coal fly ash. Silver in municipal ashes was about three times more concentrated than average levels in coal and other feedstocks, and in coal ashes, about two times more concentrated. No indication was given as to the tendency of silver to leach from the fly ash.

Agricultural Purposes: Olsen et al. (undated) used the wastewaters from two different secondary treatment plants for spray irrigation and surface flooding. The effluents contained about 0.002-0.006 ug/l Ag. No surface accumulation was noted for the site receiving spray irrigation, but was noted for silver in the top of 0-15 cm of the plot that was flooded. Figure 10 illustrates the silver concentration with respect to the soil profile. Smith and Carson (1977) stated that since silver concentrated in sludge may approach 900 mg/l, the concentration of silver in agricultural soils may be enhanced significantly when sludge is applied.

Transport: Silver in soils may be adsorbed or complexed to organic matter, clays, and iron, and manganese oxides. Mobilization in soils may be favored by good drainage, and formation of soluble organic complexes. If surface erosion occurs in areas where high silver concentrations have accumulated in the upper soil layers, then silver may be transported to adjacent soil or surface water.

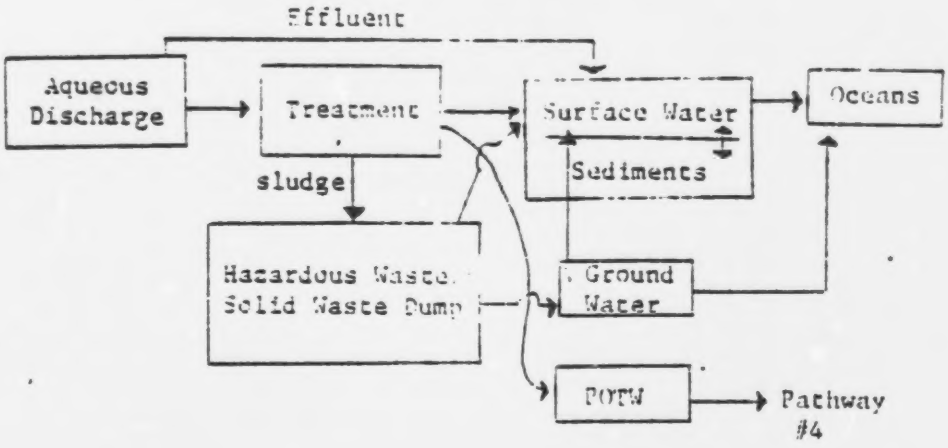


Source: Olson *et al*. (undated) Units are in mg/kg

FIGURE 10 SOIL PROFILE OF SILVER CONCENTRATIONS ON SITE RECEIVING SECONDARY TREATMENT PLANT EFFLUENT BY SURFACE FLOODING

Summary Statement: Silver in tailing ponds, abandoned mine tailings, coal pile stocks, landfills for solid and municipal waste (including photographic solid waste), and acid mine drainage has not been shown to enrich the surface and ground waters in proximity to the researched areas. In most cases, silver concentration was near or below the detection limit of the apparatus used to measure aqueous concentrations in the leachates. Therefore, the transport of silver from land to water is not expected to be significant due to leaching except under conditions favoring mobilization or under conditions of severe surface erosion. No incidents of these conditions were reported. Agricultural irrigation by surface flooding did cause surface accumulation of silver in the top few centimeters of soil. Sludge application for agricultural soil amendment might result in a similar accumulation of silver.

d. Pathway 3 - Industrial Aqueous Discharges



Sources: Silver is used industrially in the soluble form ($AgNO_3$) in ceramic paint production, photography, electroplating, ink manufacture, and for medicinal purposes. The metal is also used for production of batteries, jewelry, coinage, mirrors, contacts, and conductors. Only the photography and electroplating industries have significantly high effluent levels of silver, and so release significant aqueous discharges at least locally.

Silver recovery processes, such as smelting and refining, also release some silver to the water. The probable form of silver in photography processing effluents is the silver thiosulfate complex, $Ag(S_2O_3)_2^=$.

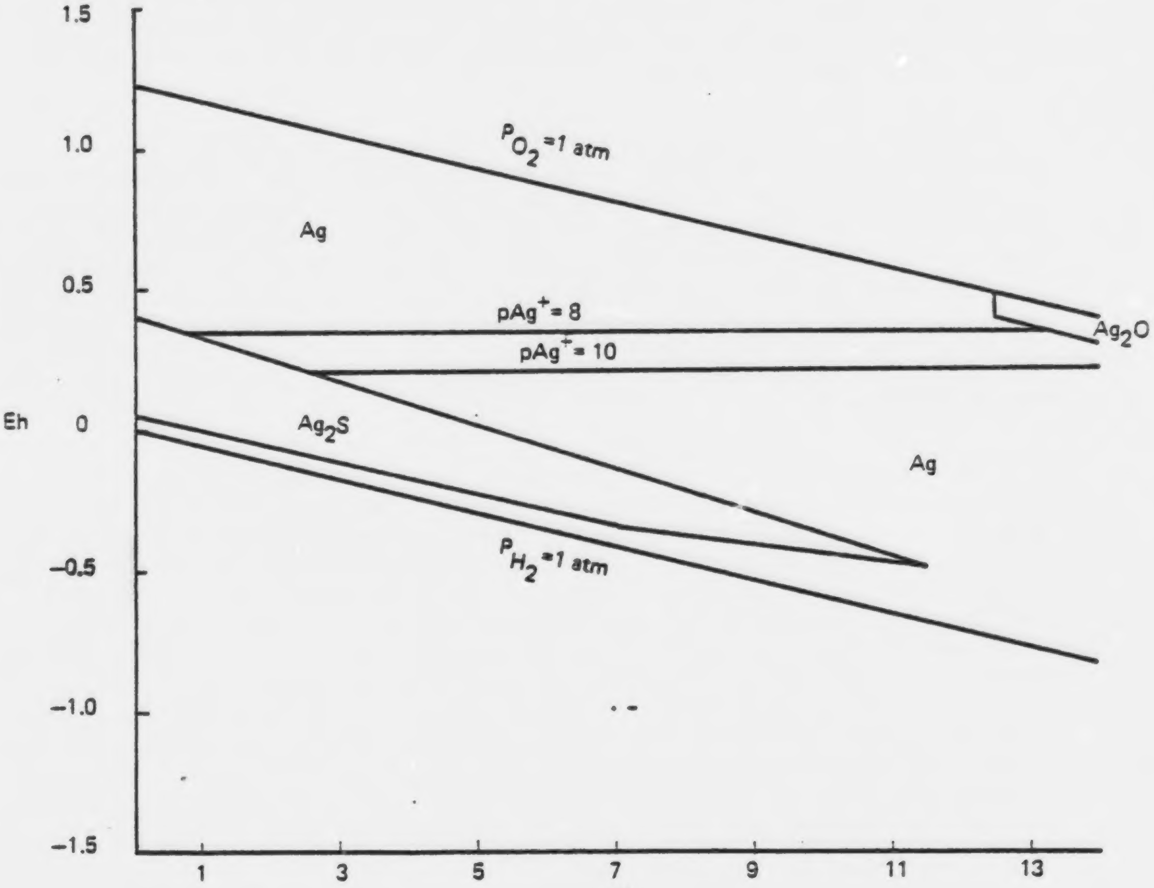
About one-half of the silver recovered from photofinishing solution originates from hypo solutions, processing emulsions, and spent film and X-rays. Two-thirds of the liquid waste containing silver results from spent fixing and bleach solutions (Smith and Carson 1977). Electroplating wastes consist of "mill wastes" (spilled and spent electrolyte) and rinse solutions. Mill wastes usually contain silver as silver cyanide and concentrations of silver average about 250 mg/l $Ag+$ in the mill wastes, and range from 50 mg/l to 250 mg/l $Ag+$ in the rinse (Smith and Carson 1977).

Forms of Silver in Surface Water: In natural waters, silver exists as $Ag+$, colloidal complexes, or as a trace element in living organisms. The equilibrium of silver between water and solid phases (e.g., soils and minerals) is influenced by the pH, the redox environment, and the presence of complexing ligands. Figure 11 illustrates the relationship between these factors for the Ag-S-O-H system. At silver ion concentrations of 10^{-8} and 10^{-10}, predominant species are AgO and AgS; silver (I) oxide is found only under conditions of high pH and redox potential and therefore is probably not an important species in terms of environmental transport.

Two recent studies offer important insight into the distribution and speciation of silver in natural waters. Jenne and co-workers (1979) have recently modeled speciation in fresh and marine waters. At silver and total sulfur (H_2S + $HS-$) concentrations of ~$10^{-1.0}$M and 10^{-9}M respectively, AgHS is an important species. In river environments where salt concentration is generally low, the concentration of AgHS is predicted to exceed that of $Ag+$ and AgCl by as much as tenfold. In marine environments, only $AgCl^{-}_{2}$ concentration is predicted to exceed that of AgHS, and "free" Ag is negligible. Kharkar et al. (1968) have estimated the flux of silver (dissolved and suspended) from freshwater streams to the ocean. Of the total stream load of approximately 0.32 ug/1, silver is supplied largely as dissolved species (~0.3 ug/1); suspended components account for approximately 10% of the total stream load (~0.02 ug/1).

Treatment Techniques: Treatment techniques to recover silver are precipitation, ion=exchange, electrolytic recovery, and reduction exchange. The efficiency of each method depends upon the initial silver concentration, the presence of other metals, and the pH.

Precipitation removes silver as silver chloride, which is soluble to the extent of 1.9 mg $Ag^{+}/1$ at 25°C in distilled water. A slight excess of chlorine reduces this value, but a large excess results in formation of a soluble silver chloride complex. Precipitation as AgCl allows selective recovery of silver from a waste containing other metal ions. Reduction of silver concentrations to 0.1 mg/l is possible by making the solution alkaline. AgCl is precipitated along with metal hydroxides. Washing the precipitate with dilute acid dissolves the metal hydroxides and leaves pure AgCl. For electroplating wastes containing cyanide, the cyanide must be oxidized in order to achieve effective silver recovery. Patterson et al. (1971) found that a ratio of 3.5 mg Cl to 1 mg CN would achieve 90-99% removal of



Source: Brookins (1978)

FIGURE 11 Eh – pH DIAGRAM FOR THE SYSTEM Ag–S–O–H

silver as AgCl. At an electroplating plant (Oneida Ltd.), chlorination-oxidation was found to result in a supernatant containing 0-8.2 mg/l Ag from a raw water containing 130-585 mg/l Ag (Eichenlaub and Cox 1954).

The photography industry has long used sulfide precipitation to recover silver. This method is no longer used to a great extent because of energy and financial costs and the fact that it does not distinguish between metals. Kodak precipitates silver from solutions containing organic acids by adding magnesium sulfate and lime, producing a silver sulfate oxide complex in the sludge (Patterson et al. 1971).

Ion exchange in a resin column is an effective process for dilute aqueous solutions. The silver is recovered by elution of silver salts or incineration of the resin. Silver in extremely dilute solutions have been removed at efficiencies up to 85.8% by cation exchange, and 91.7% by cation-anion exchange (Patterson et al. 1971). For the photography industry, this method may be uneconomical in its own right, but in combination with electrolytic recovery, silver is efficiently recovered from thiosulfate developer baths (Patterson et al. 1971). The Sperry Rand Corporation used ion exchange coupled with oxidation precipitation to recover silver from their electroplating waste (Eidness and Bergman 1956). Cation exchange columns were used for metals, while anion columns were used for CN. Column regeneration formed an acid and alkaline waste respectively. The alkaline waste was oxidized in order to eliminate the CN and when it was subsequently combined with the acid metallic waste, silver was precipitated as AgCl.

Electrolytic recovery is a treatment method for high concentrations of metal ions in the waste. It cannot operate for silver at concentrations lower than 100-500 mg/kg (Patterson et al. 1971). Generally large photofinishing industries use this method. The supernatant allows reuse of the fixer and gives a high purity silver (Smith and Carson 1977).

Reductive exchange is a treatment in which one metal is precipitated onto another metal. Usually zinc or iron are used, and the result is zinc or iron ions in solution. If enough surface area is present, such as in zinc or steel wool, about 95% removal of silver is achieved.

Aqueous Discharges: The most obvious releases of silver to the aqueous environment (most likely to POTWs) are from small amateur photofinishers, small electroplating companies, and certain photographic product manufacturers. From photofinishing, the most likely form of silver would be a thiosulfate complex. Gradual chemical degradation causes silver to be precipitated as a silver halide or sulfide.

Very little silver (as AgCN) is discharged from electroplaters. Aqueous discharge from small-to medium-sized plating shops are either placed in a lagoon from which the precipitated metals are recovered, or evaporated with the water recycled to the plating bath after treatment with $CaOH_2$ (Smith and Carson 1977). Because cyanide is also present in electroplating wastes, the restrictions on cyanide disposal also prevent much silver from being discharged. More than 50% of all plants in the silver halide, diazo aqueous, photographic chemical formulation and thermal product subcategories of the photographic products category discharge wastes directly to POTWs. Some, usually treated, wastes are discharged directly to surface water by <50% of the plants.

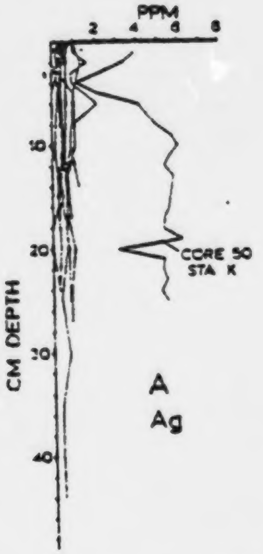
Some researchers have investigated the concentration of metals in sediments of water receiving industrial discharges. Eisler et al. (1977) studied the sediments of Narragansett Bay, which is a depository for electroplating wastes. Silver was found concentrated in the upper 5 cm of sediment. The silver concentration was lower than the concentrations of cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc, but was higher than that of cadmium. The authors compared the average sediment surface concentration of silver (1.4 mg/kg dry weight) with that for other contaminated bays and estuaries (where 0.05-1.0 mg/kg dry weight were reported).

Fink et al. (1976) determined the contamination in the St. Croix River and estuary, which receives paper mill effluent, untreated sewage, and mine runoff. No silver was detected (detection limit = 0.3 mg/kg) in the suspended solids of the St. Croix River. As revealed in Figure 12, analyses of sediment core samples also revealed low silver levels, except for the core directly downstream of the paper mill (Sta. K in the figure). The authors speculate that the silver in paper mill effluent results from the trace metal content of the trees.

Finally, sediment analysis of a highly industrialized estuary in Scotland revealed that silver levels fluctuate very little at the points of industrial inputs (Tyne, Wear Tees, and Humbar) (Talor 1979). Figure 13 indicates that the sediment silver concentration was consistently near 1 mg/kg.

Sludges: Sludges resulting from treatment of aqueous effluents for silver recovery are often treated further to recover any residual silver. The silver that is not recovered would likely be placed in a landfill or lagoon or be incinerated. The fate of silver as a result of these disposal routes is addressed in Pathway 2.

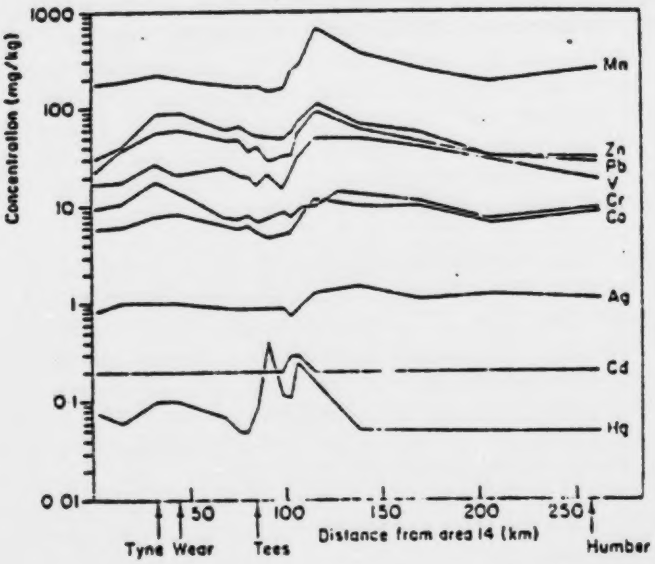
Summary Statement: Silver is discharged as an industrial waste effluent primarily by photographic product manufacturers (142 kkg), electroplaters (1 kkg), and professional and amateur photoprocessors (63 kkg). The remainder of aqueous discharges are made by smelting and refining processes (~15 kkg). Companies large enough to treat their waste effluents for silver recovery employ precipitation with chloride or sulfide, ion exhange, electrolytic recovery, and/or reductive exchange as effective treatment techniques, which are a function of the initial Ag^+ concentration. Smaller companies may use waste-holding lagoons, from which AgCl is precipitated. Amateur photographers are the most



Note: Core 50 is directly downstream from a paper and pulp plant.

Source: (Fink *et al.* 1976).

FIGURE 12 SEDIMENT PROFILE OF SILVER IN THE ST. CROIX RIVER DOWNSTREAM FROM A PAPER AND PULP PLANT



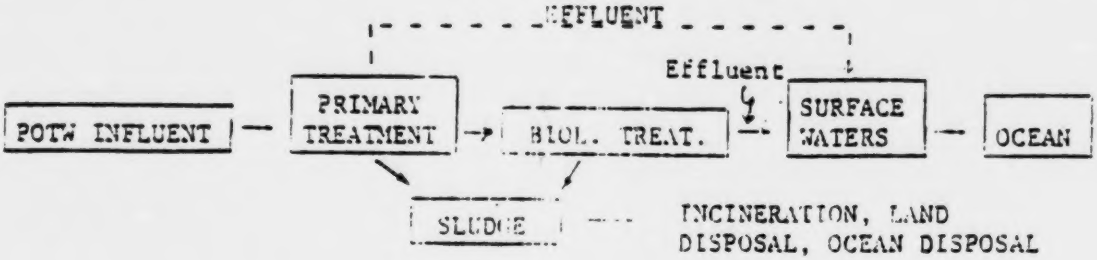
Note: Area 14 is beginning point of sampling analysis.

Source: (Taylor 1979).

FIGURE 13 DISTRIBUTION OF SILVER IN COASTAL SEDIMENTS OF THE NORTH SEA

probable dischargers of silver who do not practice recovery; the releases from this source, are estimated to total 15 kkg each year. The silver thiosulfate complex in these discharges undergoes chemical and biological degradation to form AgCl or Ag_2S.

e. Pathway 4 - POTW's



Influent: Pathway 4 describes the fate of silver entering a Publicly Owned Treatment Work. The influent to a POTW may consist of combinations of industrial effluents, domestic wastes, and surface runoff. The nature of the influent is quite varied, but Smith and Carson (1977) report most influents contain less than 0.05 mg/l Ag. Domestic wastes probably account for a small percentage of the silver entering POTWs because of discharges by amateur photographers of spent solutions down the sink. Industrial contributions would be accounted for by electroplating industries and photographic material producers.

Treatment: The degree to which silver is removed from the raw wastewater, and thus the silver concentration in the discharged wastewater, depends on the type of treatment involved. Mytelka et al. (1973) reported that for all municipal treatment plants in New York, New Jersey, and Connecticut, the incoming, as well as the outgoing waters, from primary treatment and biological treatment contained less than 0.5 mg/l Ag. Linstedt et al. (1971) investigated the effectiveness of coagulation, sedimentation, sand filters, activated carbon, and ion exchange, upon an effluent obtained from a trickling filter (Ag concentration = $\leq$ 4.6 ug/l). Fifty ug/l AgNO was added for the experiment. The percentage removed by each is as follows:

Unit Process	% Ag Removal
Cumulative Removal After Given Process	
Sand Filter	11.6
Lime Coagulation and Settling	97
Activated Carbon	97.1
Cation Exchange	98.8
Anion Exchange	99.4

Linstedt et al. (1971) concluded that activated carbon is a promising technique for removal of silver. Cation exchange, alone, removed 85.8% Ag, and coupled with anion exhchange, removed 91.7% Ag.

Supporting the results obtained by these researchers for activated carbon is the research conducted by Netzer et al. (1974) using discarded tires for metal removal from wastewaters. The tires serve as carbon surfaces (and perhaps provide sulfur to precipitate the silver), which remove the metals from the water. This researcher found that lime removed only 3% of the silver added; this is much lower than the percentage removal reported above. Subsequent introduction of tires removed more than 99.9% of the silver ion over the pH range 6-10.0.

Free silver ion is among the most toxic elements to microorganisms. Poon and Bhayani (1971) researched how organisms in activated sludge respond to slug doses of silver introduced as $AgNO_3$. Twenty-five mg/l Ag^+ (as $AgNO_3$) produced total inhibition of microorganism growth. Obviously, this concentration is far above what would be encountered in a treatment plant. Concentrations of 5 mg/l and 1 mg/l did not totally inhibit growth. However, no attempt was made to determine the amounts of silver ion adsorbed on sludge or complexed after addition. Therefore, the threshold for inhibition by free silver ion is still not well defined.

Sludge: Silver is partitioned into the sludge portion of the waste during treatment. Smith and Carson (1977) report silver concentrations ranging from 0.005 mg/kg to 900 mg/kg in sludge. This would represent up to 50% of the soluble silver, and up to 70% of the total silver, if suspended solids are included. Anaerobic digestion would retain 90% of the silver, mostly as Ag_2S.

Fortescue et al. (1975) analyzed sludge from six wastewater plants in Ontario. Three of the plants accepted principally residential wastes, and the other three were more industrial in nature. The silver concentration in the sludge ranged from 8 mg/kg to 37 mg/kg, with no clear trend developing according to the nature of the wastewater or treatment scheme. As illustrated in the pathway flow diagram, sludge may be incinerated, used for agricultural purposes, disposed of in a landfill or in the ocean. The land disposal fate of silver is covered in Pathway 2.

Effluent: Silver that is eventually discharged after treatment is in the form of silver thiosulfates, colloidal silver chloride and sulfide, and soluble organic complexes (Smith and Carson, 1977). Morel et al. (1975) used Los Angeles County sewage to study the effects of ocean disposal upon the mobility of trace metals. The sewage contained 20 ug/l of silver after primary treatment, compared with the seawater concentrations of 0.3 ug/l. The speciation and mobility of the metals were studied by use of an aqueous chemical equilibrium model, REDEQL, which has the capability of modelling inorganic and organic complexation, and surface adsorption. For all three model options, it was predicted that 100% of the silver would be present as Ag_2S. The authors generalized for all metals that dilution and oxidation of the sewage at the outfall would permit only about 1% of the metals to be deposited in that area.

Summary Statement: According to one study, the concentration of silver entering a POTW is quite low (<0.05 mg/l). The average influent level reported in Chapter III was 0.008 mg/l. Treatment techniques that appear to be particularly effective in removing silver from wastewater are lime and settling (97% removal), activated carbon (>97% removal) and cation-anion exchange resins (91.7% removal). The average treated effluent level from the same study reported in Chapter III was 0.002 mg/l.

Silver is partitioned into sludge for which maximum concentrations of 900 mg/kg and more typical levels of 100 mg/kg have been reported. In anaerobic sludges, approximately 90% of the silver will be partitioned with the sludge. Although silver is toxic to microorganisms, it is unlikely that concentrations will approach those inhibiting growth. One study found that the organisms in activated sludge were only slightly inhibited at nominal concentrations of 1-5 mg/l $AgNO_3$.

D. BIOLOGICAL FATE

1. Aquatic Organisms

Fish, aquatic invertebrates, and plants may accumulate silver from either water or sediment. According to the preceding section, water concentrations are usually low, while sediments serve as a reservoir of silver, especially in the vicinity of sources. Most laboratory studies are concerned with uptake from filtered water, with no consideration of the role of the sediment burden in regard to bioaccumulation, even though certain bottom dwellers, such as shellfish and scavenger fish, would have considerable contact with these silver sources. However, due to the limitations of available data, the following discussion is of bioaccumulation by aquatic organisms, usually involving only dissolved or suspended forms of silver.

The biological action of silver may involve reversible chemical bonding with enzymes and other active molecules at cell surfaces. The lipid phase of the cell membrane appears to play an important role in the absorption of silver ions by living cells (Cooper and Jolly 1970).

a. Animals

Table 24 presents the levels of silver that have been reported to accumulate in a number of aquatic animals. The ratio of accumulated concentration to exposure concentration from experimental work by Coleman and Cearley (1974) ranges from 2.4 to 333 for bass and bluegills. Internal organs and gills concentrated greater levels of silver than did the remainder of the body. Davies et al. (1978) feel that Coleman's results are understated due to the use of relatively hard water with an atypically high chloride concentration (Davies et al. 1978). Higher levels of silver (up to 4,400 mg/kg in bone) were accumulated by cut-throat trout, while marine organisms such as oysters accumulated 189 mg/kg. No correlation was observed between size and weight of red abalone and accumulated silver concentration (Anderlini 1974).

Enrichment factors as high as 22,000 have been calculated for marine animals. Marine animals (containing 1.0 mg/kg dry matter) accumulated 3,300 times the silver content of seawater, while freshwater animals (containing 0.40 mg/kg dry matter) have been reported to concentrate silver by a factor of 3,080 (Smith and Carson 1977).

Shellfish, particularly oysters, passively accumulate many metals much more readily than fish (Phillips and Russo 1978). Silver is not likely to be bioaccumulated in freshwater fish muscle and marine fish muscle, but it is considered likely to be bioaccumulated in marine shellfish or crustaceans (Phillips and Russo 1978). A study of fish and silver concentrations in German rivers concluded that the bioaccumulation factor (BCF) for fish flesh is inversely proportional to the silver concentration in water. The BCF was approximately 9 at a concentration of 0.1 ug/l silver, while at 10 ug/l silver, the BCF was reduced to approximately 0.20 (Feldt and Melzer 1978).

Coleman and Cearley (1974) found that the main site of silver intake in bluegill is the gills. Silver accumulation was greatest in the internal organs of large-mouth bass. After 2 months of exposure to silver, equilibrium developed between the concentration in the water and in the fish tissue. These authors have hypothesized that the absence of significant additional accumulation after 2 months could be related to the mechanisms affecting uptake and elimination. They postulated that the mechanisms affecting elimination may have been stimulated so that uptake rate approximated elimination. The study cited an investigation in which $Ag^{203}$was found to accumulate in large amounts in the kidney and liver tissues of goldfish. The authors found that juvenile large-mouth bass and bluegills exposed to 0.01 mg/l or 0.001 mg/l for 6 months continued to accumulate silver for 2 months and then leveled off. The internal organs contained more silver than the muscle tissue. The 1974 study by Coleman and Cearley found gills and internal organs from bass reaching much higher silver levels than the remaining tissue.

TABLE 24. ACCUMULATION OF SILVER IN AQUATIC ANIMALS

Species	Organ	Conditions	Exposure Concen- (ug/1)	Accumu- Concen- (ug/1 dry)	Accumulated Exposure ("BCF")	Reference
FRESHWATER						
Largemouth Bass Micropterus salmoides	Body Remainder	Moderately Hard Water (180 mg $CaCO_3$/1) 4 months	0.3 (control)	0.0012 (Ash Wt.)	.4	Coleman and Cearley (1974)
			0.9	0.009	10	
			7.0	0.017	2.42	
	Internal Organs		0.3	0.050	166	
			0.9	0.300	333	
			7.0	0.600	85.7	
	Gills		0.3	0	0	
			0.9	0.220	244	
			7.0	0.370	52.86	
Bluegill Lepomis Machrochirus	Total Body		0.3	0.003	8.33	Coleman and Cearley (1974)
			0.9	0.008	8.33	
			7.0	0.040	5.71	
			70	0.250	3.57	
		28 days	.03	0	0	U.S. EPA (1979)

Tables 24 and 25 also indicate the organs where bioaccumulated levels were high. Cut-throat trout from an Alpine lake located in a region undergoing extensive cloud seeding with silver iodide was found to contain the greatest concentrations of silver in liver and bone tissue. The marine fish species, dover sole, exposed to silver-contaminated wastewater in an outfall off the coast of California was also observed to contain higher concentrations of silver in the liver as compared with the flesh (McDermott _et al_. 1976).

Silver is accumulated by the hepatopancreas and nephridial organs of brachiopods, mollusks, and arthropods (particularly Crustacea) (Smith and Carson 1977). Silver is concentrated in the glandular tissue of the liver of fish and most vertebrates (Smith and Carson 1977).

The rate of silver uptake by Japanese eel (_Anguilla japonica_) and goldfish (_Carassium auratus_) was determined to be 1.2-4.2 x 10^{-7} mg/hour from a 0.74 mg/l solution of radiosilver sulfate (Ag^{110}) (Smith and Carson 1977).

The bioaccumulation of silver is affected by those parameters that affect the biological action of silver compounds. Behavior of silver compounds in water is strongly affected by temperature, oxygen concentration, the presence or absence of other cations, and pH. Also, since information on antagonistic and synergistic effects is lacking in much of the published work, it is difficult to evaluate the influence of such effects on the results of many experiments reported in the literature (Cooper and Jolly 1970).

b. Monitoring Data

Surveys of the tissue concentrations of metals in fish from both marine and freshwater environments show that silver is usually present in low concentrations, usually less than 100 mg/kg (Phillips and Russo 1978).

Trout in unpolluted environments have been shown to contain concentrations of silver comparable to those in fish in more polluted areas (see Table 25). Tong _et al_. (1974) studied trout in Cayuga Lake (NY) at ages between 1 year and 12 years. They reported levels ranging from 0.68 ug/kg to 0.48 ug/kg, with steadily decreasing levels with age. Somewhat higher levels, with an average concentration of 0.57 mg/kg for all body parts, were reported by Freeman (1977) for trout in an alpine lake in Colorado. Although the lake was in an isolated area, there was the possibility of some contamination from cloud seeding with AgI.

Greig and Wenzloff (1977) collected several species of finfish from marine waters in Long Island Sound and the New York Bight in the vicinity of dredge spoil and sewage sludge disposal sites. Levels in fish muscle and liver were similar among the different species sampled, ranging from

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TABLE 25. SILVER CONCENTRATIONS DETECTED IN AQUATIC BIOTA

Description of Species	Concentration (mg/kg) Mean	Concentration (mg/kg) Range	Reference
Colorado Alpine Region - Trout			
muscle	0.29	ND- .99	Freeman (1977)
fat	0.01	ND-0.04	
liver	1.81	0.94-3.65	
Cayuga Lake, N.Y. - trout			
1-6 years of age	0.00068 (wet)		Tong et al. (1974)
7-8 years of age	0.00048 (wet)		
9-11 years of age	0.00058 (wet)		
12 years	0.00048 (wet)		
Long Island Sound/N.Y. Bight - finfish	0.19	0.1 - .8 (wet)	Greig and Wenzloff (1977)
- windowpane flounder	0.1		Greig et al. (1977)
- rock crab	0.39	0.24-0.79 (wet)	Greig et al. (1977)
Southern California outfall - Dover sole			
control	0.3		McDermott et al. (1976)
outfall	0.2		
Alpine Lake contaminated by Cloud Seeding - cutthroat trout (various organs)		0.09-4.4	Goettl et al. (1974)
North Atlantic scallops - muscle	0.12 (wet)	0.97-0.24	Greig et al. (1978)
- total mass	0.51 (wet)	0.22-1.9	Greig et al. (1978)
North Atlantic - surf clam	0.8	0.39-1	Greit (1975)
North Atlantic marine clam - Rhode Island	2.34 (dry)	1.16-4.64	Eisler (1978)
Mid-Atlantic scallops	1.80 (dry)	0.39-9.08	Pesch et al. (1977)
England clams - contaminated estuary	0.57 (dry)	0.23-1.2	Bryan and Hammerstone (1978
- non-contaminated estuary	0.4	0.37-0.6	Bryan and Hammerstone (1978

TABLE 25. SILVER CONCENTRATIONS DETECTED IN AQUATIC BIOTA (continued)

	Concentration (mg/kg)		
Description of Species	Mean	Range	Reference
California - mussels (whole body)			
polluted area	0.6		Martin (1979)
unpolluted area	0.18		Martin (1979)
- oysters (gills)			
polluted area	189		
unpolluted area	3.7		
California Coast - Red abalone gill, mantle, foot and digestive gland		0.130-129	Anderlini
Philadelphia near acid water - sea scallop and sewage sludge disposal area whole body	1.8	0.43-9.08	Pesch *et al.* (1977)
Los Angeles - rock scallop (digestive gland)			Young and Tsu-Kai (1979)
outfall area	2.0		
control area	0.02		

less than 0.1 mg/kg to 0.8 mg/kg, and averaging 0.19 mg/kg. In a study of the same area, Greig et al. (1977) reported silver levels of less than 0.1 mg/kg in flounder and an average of 0.39 mg/kg in rock crab.

In a study of Dover sole in southern California, McDermott et al. (1976) reported an average silver concentration of 0.2 mg/kg in the vicinity of a municipal waste outfall; samples taken in a control area had levels higher than those at the outfall, 0.3 mg/kg. It appears that there is very little difference between silver concentrations in fish living in enriched and unpolluted environments.

Background silver levels have been published for a number of marine animals. The jellyfish has been observed to contain 2.8 mg/kg (dry weight) while sea anemones are reported to have 6.0 mg/kg (dry weight). The soft parts of an oyster have been observed to contain 4.5-73 mg/kg. Detectable amounts of silver have been found in the ash of crabs and fish (Cooper and Jolly 1977). Silver burdens of 2.6-7.1 mg/kg (dry weight) have been reported for the saltwater worm, Neris diversicolor, from sediments with almost the same concentrations (Lockwood 1976). Silver residues in the liver of the Greater Scaup seaduck (Aythya marila) were found to be .04-.032 mg/kg (wet weight) near Vancouver, B.C.; this concentration is one order of magnitude greater than the level in the food of these birds (Vermeer and Peakall 1979).

Silver concentrations in scallops, crabs, and other marine biota consistently are reported at values similar to those for fish. Greig et al. (1978) collected sea scallops along the North Atlantic Coast and reported an average concentration of 0.12 mg/kg silver in muscle tissue. In a similar, earlier study Greig (1975) reported silver levels in North Atlantic clams and crabs of 0.8 mg/kg and 1.8 mg/kg respectively.

Clams were collected in the vicinity of an electroplating firm during the fall of 1973 in Narragansett Bay, Rhode Island, by Eisler et al. (1977). They reported a mean concentration of 2.34 mg/kg, with a range of 1.16 to 4.64 mg/kg. Pesch et al. (1977) reported levels averaging 1.8 mg/kg in scallops inhabiting the area in and around a mid-Atlantic disposal site, and Bryan and Hummerstone (1978), in an examination of burrowing clams in a contaminated and an uncontaminated estuary, recorded only slightly higher levels in the contaminated sample area; 0.57 mg/kg and .4 mg/kg respectively.

In conclusion, it appears that silver content in aquatic animals is negligibly affected by high pollutant concentrations in their habitat. Silver levels range from less than 1 ug/kg up to 9.08 mg/kg with most reported concentrations falling between 0.1 mg/kg and 0.9 mg/kg.

Table 26 summarizes the silver concentrations found in fish tissue in different basins of the U.S., with maximum concentrations ranging from 0.02 mg/kg to 1.9 mg/kg.

TABLE 26. STORET DATA ON SILVER CONCENTRATIONS IN FISH TISSUE

	Concentrations (ug/kg)														
	1975			1976			1977			1978			1979		
Basin	Max.	Min.	(No.)	Max.	Min.	(No.)	Max.	Min.	(No.)	Max.	Min.	(No.)	Max.	Min.	(No.)
1. Northeast	690	90	(72)	120	120	(1)									
2. North Atlantic	1900	70	(51)	230	110	(2)									
3. Southeast	820	80	(8)												
5. Ohio River	500	500	(7)												
7. Upper Mississippi										60	50	(9)			
9. Missouri River										50	50	(11)	70	50	(10)
10. Lower Mississippi							104	104	(1)	650	50	(4)			
12. Western Gulf							210	210	(1)	400	400	(1)			
13. Pacific Northwest							200	200	(1)	1000	4	(27)	30	20	(9)
16.										20	20	(6)			

	Max.	Min.	(No.)	Mean
Gross	1900	4	221	235

Source: U.S. Environmental Protection Agency, STORET (1980).

c. Plants

The reported background silver concentrations in aquatic plants vary widely (Cooper and Jolly 1970): 0.2 mg/kg silver (dry weight) for diatoms, 0.2-0.8 mg/kg for algal species.

Marine plants (from water with an unspecified silver content) have been reported to contain up to .060 mg/kg silver (dry weight) and most freshwater plants up to 0.026 mg/kg; both concentrate silver by a factor of 200 (Smith and Carson 1977). Silver residues in vascular marine plants near British Columbia contained 0.01-0.48 mg/kg silver (wet weight) (Vermeer and Peakall 1977).

The freshwater water hyacinth (*Eichnomia crassipies*) and alligator weeds (*Altemanthera philoxeroides*) have been observed to absorb 650 mg/kg and 440 mg/kg (dry weight) silver per day, respectively (Wolverton *et al*., undated). Concentrations of silver in water were not reported.

2. Terrestrial Organisms

a. Animals and Plants

In general, mammals do not accumulate much silver because of the low solubility of most silver compounds and because of a generally low rate of absorption through body membranes (Phillips and Russo 1978). Table 27 presents the background concentrations of silver in tissue of terrestrial animals. One study concluded that the chronic accumulation of silver in the rumen of ruminant species is unlikely because most of the administered silver passed to the rumen is in insoluble form (U.S. EPA 1979).

Table 28 presents the background concentrations of silver in terrestrial plants. The background silver content of plants ranges from 0 mg/kg to 2.4 mg/kg, although silver is not an essential constituent of plants (Smith and Carson 1977).

Plants appear to contain silver in concentrations similar to those found in aquatic biota, levels falling primarily between 0.03 mg/kg and 4.3 mg/kg (Young *et al*. 1973), There is a large seasonal variation in silver concentration of common juniper and club moss; from 5 to 50 times larger amounts are found in the spring compared with those in the fall, most likely due to seasonal changes in the plants' chemical composition (Horovitz *et al*. 1974). Young *et al*. (1973) reported the widest range in concentrations, 5.5 mg/kg. In food crops, Vanselow (1966) reported levels ranging from less than 0.2 mg/kg to 2 mg/kg in tea and Cooper and Jolly (1970) reported concentrations of "up to several hundred mg/kg (dry weight)." Among other edible plants that concentrate silver are Mentha and Dioscorea (Smith and Carson 1977).

TABLE 27. BACKGROUND CONCENTRATIONS OF SILVER IN TERRESTRIAL ANIMALS

Species	Organ	Accumulated Silver (mg/kg)-(Dry)	Reference
Mollusc Land Snail (*Unio mancus*)	Shell	0.16-0.8	Bowen (1966)
	Flesh	0.05-0.7	Bowen (1966)
Mammals	Bones (Apatite)	0.01	Bowen (1966)
	Soft Tissue	0.005-0.04	Bowen (1966)
Ducks	Tissue	0.04[1]-2.0	Vermeer and Peakall (1979) and Bagley and Locke (1967)

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[1] Wet weight.

TABLE 28.

SILVER CONTENT OF TERRESTRIAL PLANTS

Species	Accumulated Ag (mg/kg Dry Weight)	Ag in Soil (mg/kg)	Reference
BACKGROUND CONCENTRATIONS			
Common juniper (*Juniperus communis*)	May: 1.5 Sept: 0.02	0.09 (Exposed land of a botanical garden)	Horovitz *et al* (1974)
Club moss (*Lycopodium circinatum*)	May: 1.0 Sept: 0.02	0.03 (Greenhouse of a botanical garden)	Horovitz *et al* (1974)
Gymnosperms	0-1.4 (0-3.0 in ash)		Cooper and Jolly (1970)
Alfalfa (*Medicago sativa*)	0.02-1.3 in tops	Field grown	Smith and Carson (1977)
Wheat (*Triticum sp.*)	0.5 1.0 in bran		Smith and Carson (1977)
Mushroom (13 species)	average: 1.4 range: 0.03-5.5	average 1.0 (unpolluted area in Norway)	Allen and Steinnes (1978)

TABLE 28. (continued)

SILVER CONTENT OF TERRESTRIAL PLANTS

Species	Accumulated Ag (mg/kg dry weight)	Ag In Soil (mg/kg)	Reference
EXPERIMENTAL			
Grass			
2-1/2 years after application of:			
100,000 mg/kg NO_3	46,500	16,610.	Klein and Molise (1975)
1,000 mg/kg NO_3	1,800	483	Klein and Molise (1975)
100,000 mg/kg AgI	3,580	20,530	Klein and Molise (1975)
1,000 mg/kg AgI	10	285	Klein and Molise (1975)
Cactus			Klein and Molise (1975)
100,000 mg/kg NO_3	1,740	16,610	Klein and Molise (1975)
1,000 mg/kg NO_3	100	483	Klein and Molise (1975)
100,000 mg/kg AgI	840	20,530	Klein and Molise (1975)
1,000 mg/kg AgI	30	285	Klein and Molise (1975)
Bush Beans	1,760 0 roots*		Wallace and Romney (1977)
(*Phaseolus vulgaris*)	5,1 stems		
13 days in 10^{-5} M $AgNO_3$	5.8 leaves		

* Wallace (1979) reports 760,000 for roots.

Experimental data show that grasses have higher relative silver concentrations than cactus, but that both species accumulate approximately one-tenth of the soil concentrations resulting from Ag treatments. Grasses had higher silver concentrations than soils following $AgNO_3$ treatment. Klein (1975) concluded that silver from $AgNO_3$ will be taken up by plants to a greater extent than from AgI, but that with increasing concentration of silver in soil, more silver is localized in roots than in above-ground plant parts.

The ash of terrestrial plants usually contains 0.2 mg/kg of silver, with the highest concentration in seeds, nuts, and fruit (Smith and Carson 1977), 0.400 mg/kg has been detected in whole wheat, and 0.800 mg/kg have been detected in wheat germ (Smith and Carson 1977).

The availability of silver in soil for plant uptake depends on the pH of the soil solution. At about pH 7, silver ion concentration in soil solution is less than 0.05 mg/kg. At pH 5 to 6, the concentration increases, and at pH 7.5 to 8.5, the concentration decreases. In a study in Colorado, soils with a high silver concentration exhibited lower pH, higher water content, respiration rate, and concentration of organic matter with increasing silver iodide content up to 50 mg/kg, and greater numbers of microorganisms. Adsorption and complexing of silver by soil humates would tend to inhibit their decomposition and lessen the toxic effect of silver on soil microorganisms (Smith and Carson 1977).

Bioaccumulation of silver by plants may be influenced by the presence of other heavy metals. Preferential uptake of copper over silver has been observed in white oak trees (Quercus alba): Cu/Ag ratios were greater in the twigs than in the surrounding soil (Leavitt et al. 1979).

b. Biomagnification in the Food Chain

There seems to be little likelihood that silver will be increased through terrestrial food chains to a level that is dangerous to higher organisms (Cooper and Jolly 1970). Aquatic organisms seem to have a greater ability to bioconcentrate silver than terrestrial mammals. This may be due to uptake through a greater number of and more efficient exposure routes (e.g., gill absorption, better gut absorption efficiency).

c. Microorganisms

Bacterial populations may accumulate high levels of silver, especially groups acclimated to silver concentrations. Up to 300 mg/g (dry weight) of silver was measured in a 3-species bacterial population growing in a chemostat (Charley and Bull 1979). An uptake rate of 21 mg silver h^{-1} (g biomass)$^{-1}$ was measured; the extent of removal of silver from water was concentration-dependent. Pseudomonas maltophilia comprised 50% by numbers of the community and was particularly resistant to the toxic effects of silver. The authors suggested that exposure of multispecies communities of bacteria could be used in the wastewater treatment of silver as a removal process.

The more commonly observed effect of silver on microorganisms, however, is toxicity; investigations of this subject are discussed in Section V-B. Not enough information is available to assess the likelihood that natural populations of microorganisms would accumulate silver rather than be inhibited by typical environmental levels of silver. If the propensity for microbial bioaccumulation is common in the environment, then there are situations where microorganisms may serve as a significant reservoir of silver (e.g., in systems with high biomass such as eutrophic lakes, estuaries, etc.).

E. CONCENTRATIONS DETECTED IN THE ENVIRONMENT

1. Surface Water

Annual mean concentrations of silver in surface water in the U.S. have ranged from 1 ug/l to 9 ug/l during the period 1970 to 1979. Maximum concentrations of silver over the same time period ranged from 94 ug/l to 790 ug/l. Figure 14 exhibits the trends in maximum and mean silver concentrations in the United States from 1970 to 1979.

The distribution of silver concentrations in surface water is given in Table 29. The majority of "unremarked"[1] observations between 1970 and 1979 were for concentrations of 0-1 ug/l. From 78% to 98% of all observations in a given year for this period were for concentrations of less than 10 ug/l.

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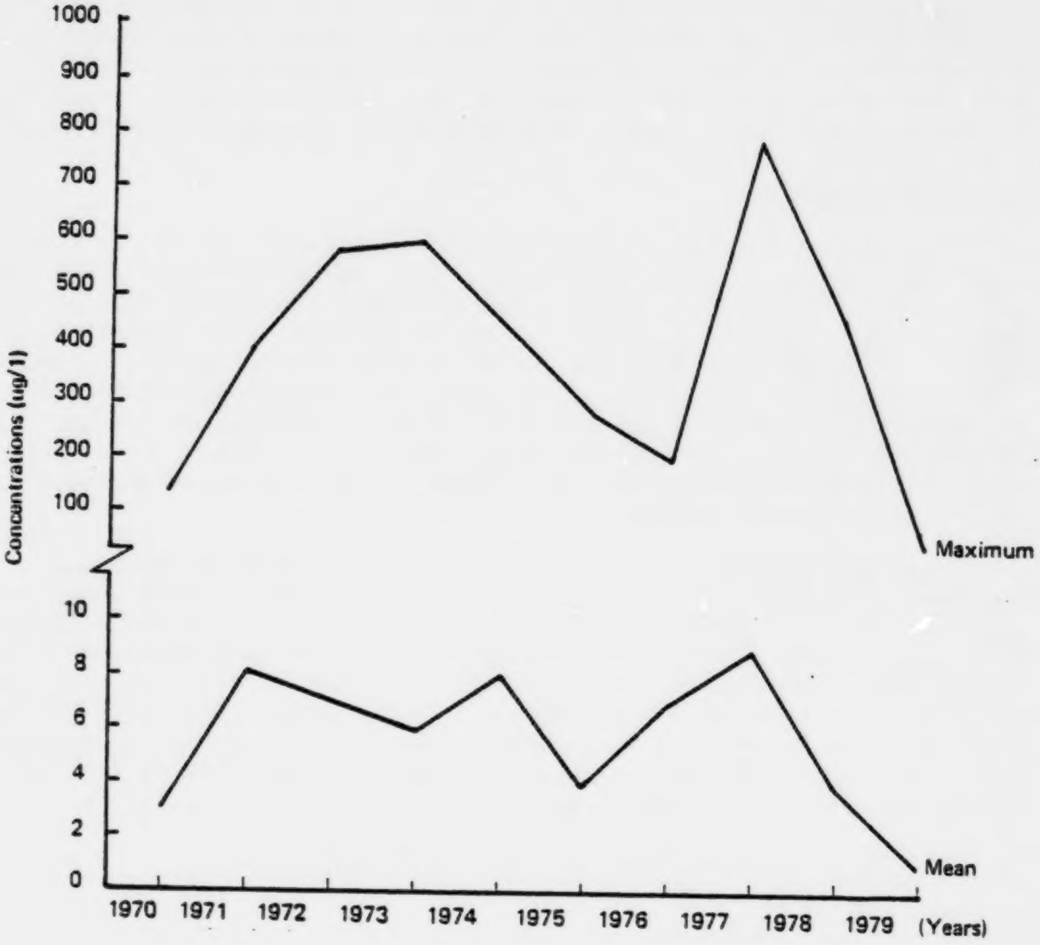
[1] Unremarked data are observations above detection limits.



Source: U.S. Environmental Protection Agency, STORET, 1980.

FIGURE 14 TRENDS IN MEAN AND MAXIMUM SILVER CONCENTRATIONS IN SURFACE WATERS OF THE UNITED STATES, STORET, 1970–1979

TABLE 29. DISTRIBUTION OF SILVER CONCENTRATIONS IN U.S. AMBIENT WATERS, STORET, 1970-1979

Year	Number of Unremarked Observations	Percent of Observations at Concentration (ug/l)			
		0-1	1.1-10	10.1-100	100.1-1000
1970	167	92	2	5	1
1971	518	78	9	13	1
1972	1,048	74	17	8	1
1973	879	81	12	6	1
1974	960	65	22	12	1
1975	1,436	69	24	8	0
1976	2,468	56	29	15	0
1977	2,033	49	29	21	1
1978	3,054	75	18	7	0
1979	3,047	89	9	2	0
Average	-	72.8	17.1	9.7	0.6

Source: U.S. Environmental Protection Agency, STORET (1980).

The ratio of silver concentrations (total Ag) to the EPA Water Quality Criterion for protection of freshwater aquatic life is presented in Figure 15, aggregated by U.S. county. Remarked data are set to 0 and 85th percentiles are reported. Appendix B includes maps of the distribution using remarked data, and for the 50th percentile. States in which concentrations exceed the water quality criterion include Washington, Idaho, Colorado, Wisconsin, Oklahoma, California, Ohio, West Virginia, North Carolina, Pennsylvania, Maine, Louisiana, Mississippi, and at scattered locations throughout the remaining states.

Monitoring data were disaggregated for the major river basins in order to discern regional variations in silver concentrations. When the data were grouped in this manner, five of the 18 continental basins had annual mean surface water concentrations of silver exceeding the 1975 EPA National Interim Water Standard of 50 ug/l. However, the standard was not actually in effect until June 1977, while most instances of annual means exceeding 50 ug/l occurred between 1971 and 1973 as shown in Table 30. While four basins exceeded this level once during the ten years, the Northeast basin did so from 1971 to 1973 and again in 1976. Recently, very few basins have had annual mean concentrations exceeding the standard (in fact, none during 1977 to 1979).

A more realistic picture of regional variations in silver concentrations may be gathered from Figure 16. For the ten-year period, 1970-1979, the percentage change in annual mean concentrations of silver in major river basins was calculated using the difference between the combined mean for the first 5 years (1970 to 1974) and that for the second 5-year period (1975 to 1979). Too few data were available to allow this comparison for five basins--Lake Erie, Colorado River and Great Basin, Lake Huron, and Hudson Bay. Figure 16 indicates that levels of silver in 10 of the 13 basins shown, or 77%, have decreased over the past 5 years. Considering individual basins, silver concentrations decreased by 23% to 98% and for the United States as a whole, by 55% during the 1975-1979 interval. The concentrations in the North Atlantic, Southeast, and Lower Mississippi basins have increased by 420%, 300%, and 300%, respectively. Still, even with these increases annual mean concentrations of silver in these basins do not exceed the EPA Interim Drinking Water Standard.

2. Well Water

Silver concentrations in well waters are fairly uniform across the country, as reflected in observations in STORET. Of the 2,232 observations recorded from 1977 to 1979, the maximum concentration was 30 ug/l, with the mean around 14 ug/l. Table 31 exhibits silver concentrations in well waters in the major river basins from 1977 to 1979. In no case, however, was the Interim Drinking Water Standard (50 ug/l) violated.

Bradford (1971) investigated trace elements in the water resources of California. Silver concentrations in well waters at the San Joaquin Valley and in the area surrounding the Salton Sea ranged from less than 0.1 ug/l to 0.4 ug/l.

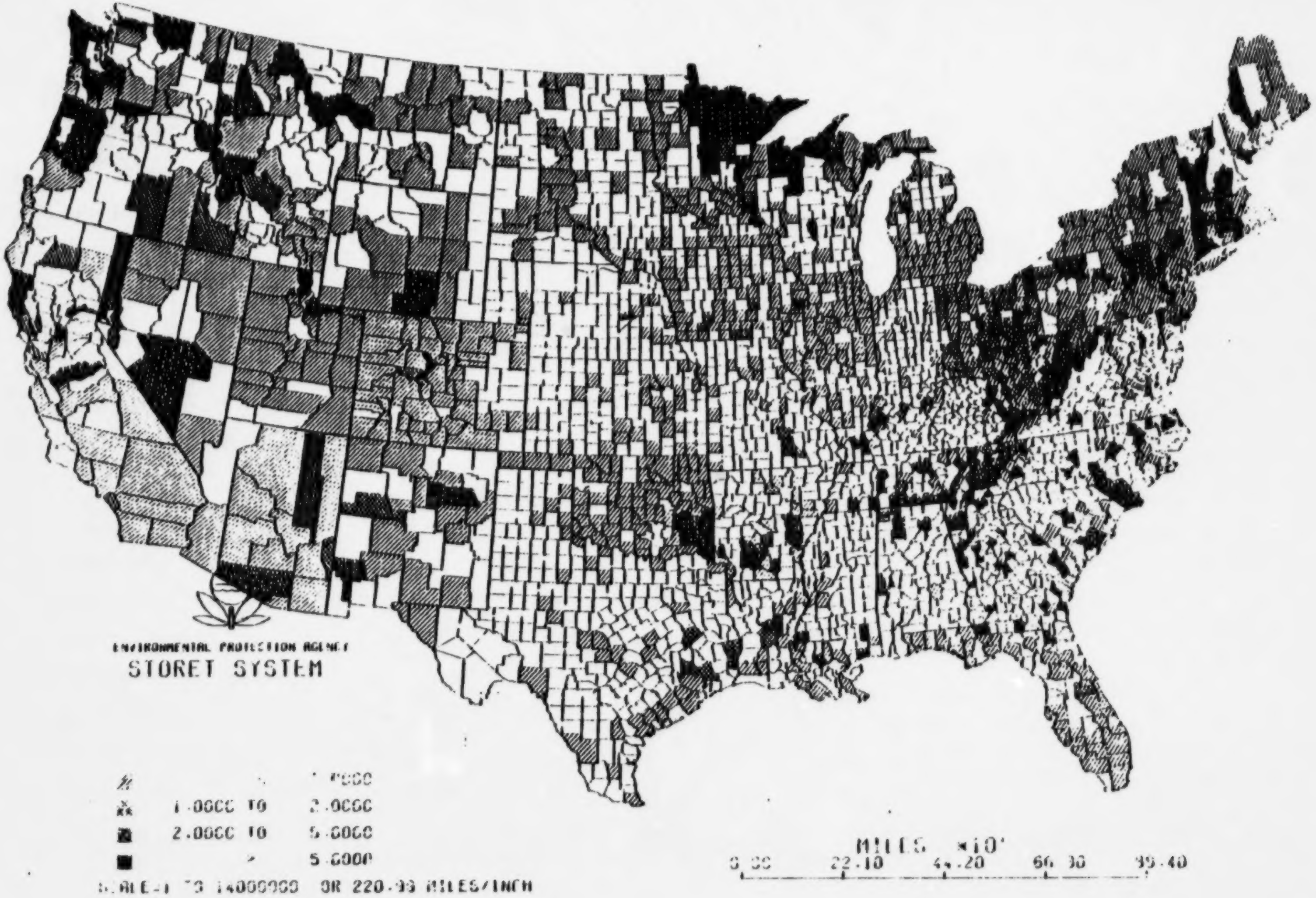
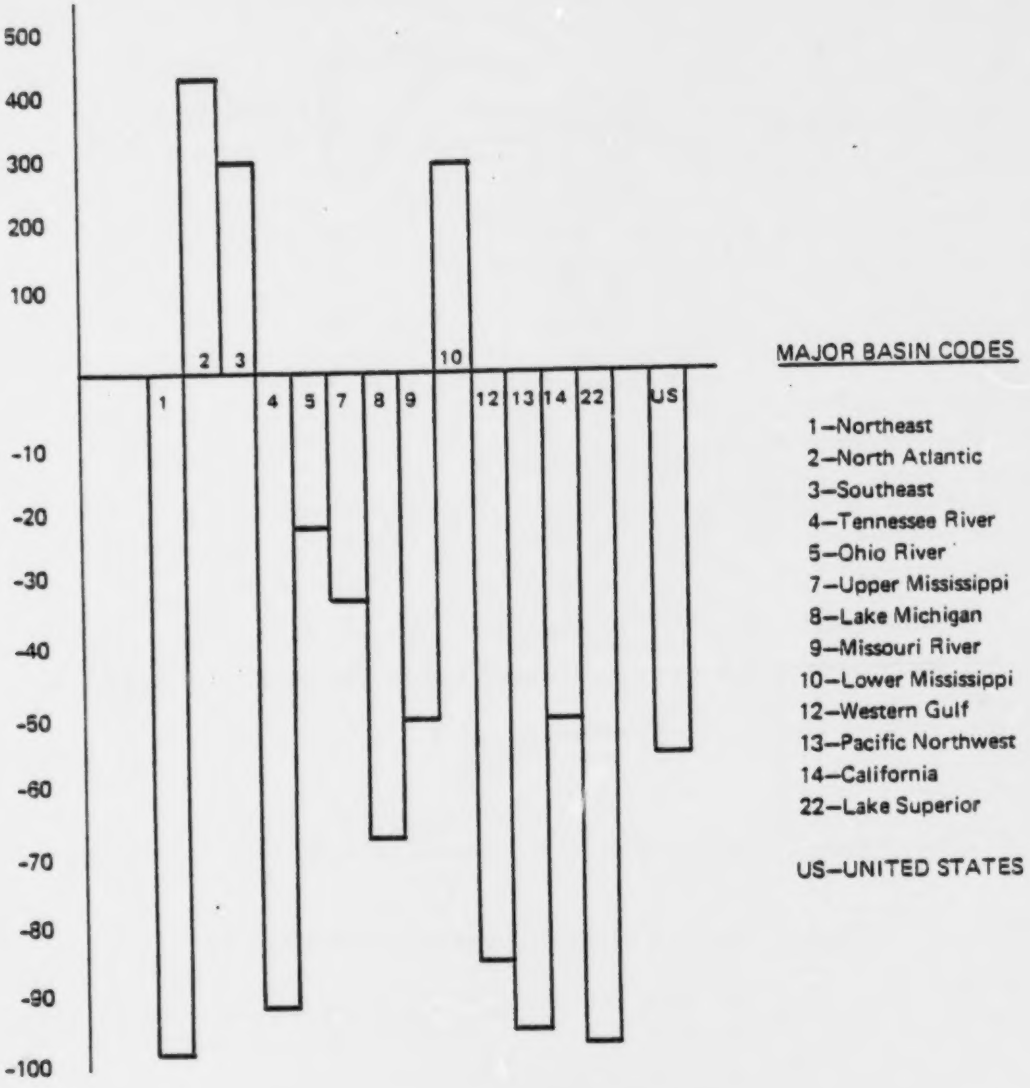

ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
< 1.0000
1.0000 TO 2.0000
2.0000 TO 5.0000
> 5.0000
SCALE-1 TO 14000000 OR 220.96 MILES/INCH
MILES ×10¹
0.00
22.10
44.20
66.30
88.40

FIGURE 15. RATIO OF AG CONCENTRATION IN WHOLE WATER TO CRITERIA AGGREGATED BY COUNTY 85 %TILE USING REMARK CODES 85TH PERCENTILES

TABLE 30. MAJOR U.S. RIVER BASINS IN WHICH ANNUAL MEAN CONCENTRATION OF SILVER IN SURFACE WATER EXCEEDED 50 ug/1, STORET, 1970-1979

Basin		Year									
		1970	1971	1972	1973	1974	1975	1976	1977	1978	1979
1	Northeast		X	X	X			X			
2	North Atlantic										
3	Southeast										
4	Tennessee River				X						
5	Ohio River			X							
6	Lake Erie										
7	Upper Mississippi										
8											
9											
10	Lower Mississippi										
11	Colorado River										
12	Western Gulf			X							
13	Pacific Northwest										
14	California		X								
15	Great Basin										
21	Lake Huron										
22	Lake Superior										
23	Hudson Bay										

Source: Arthur D. Little, Inc. based on U.S. EPA STORET.



Source: Arthur D. Little, Inc., based on U.S. EPA STORET.

FIGURE 16 PERCENTAGE CHANGE IN SILVER CONCENTRATIONS IN AMBIENT WATERS OF MAJOR U.S. RIVER BASINS, STORET, 1970–1974 PERIOD VERSUS 1975–1979 PERIOD

TABLE 31. SILVER CONCENTRATIONS DETECTED IN WELL WATERS, STORET, 1977-1979

	Major River Basins	Number of Observations	Concentrations (ug/1) Maximum	Mean
1	Northeast	27	8	5
2	North Atlantic	27	10	9
5	Ohio River	1,448	30	16
6	Lake Erie	632	30	13
7	Upper Mississippi	69	30	10
8	Lake Michigan	5	30	16
10	Lower Mississippi	1	10	10
13	Pacific Northwest	14	2	2
14	California	1	0	0
21	Lake Huron	1	30	30
22	Lake Superior	2	25	15
23	Hudson Bay	5	5	5
	UNITED STATES	2,232	30	14

Monitoring stations reporting -2,206. Includes remarked and unremarked data.

Source: U.S. Environmental Protection Agency, STORET, 1980.

The STORET data file for 1977 through 1979 contains information on silver in sediments from one-half of the major river basins in the U.S.

In a study of metal levels in ground water in the Colorado Front Range mineral belt, a total of 149 samples were collected over an area of approximately 2,070 square kilometers (800 square miles), both within and outside the mining area (Klusman and Edwards 1976). Average silver concentrations in samples from the mineral belt and outside were measured at 0.55 ug/l and 0.77 ug/l, respectively. The higher silver concentration for the non-mineral belt is labeled as suspect because of a single high value, which may be invalid. In both cases, however, silver concentrations were lower than the Water Quality Standard of 50 ug/l.

3. Sediment

The STORET data file for 1977 through 1979 contains information on silver in sediments from ½ of the major river basins in the U.S. These basins were selected to be representative of all regions of the country. During this 3-year period, maximum concentrations of silver in sediment ranged from 1 mg/kg to 95 mg/kg and mean concentrations from 1 mg/kg to 10 mg/kg. Silver concentrations in sediment are displayed in Table 32 for the reporting basins and the United States. In general, silver concentrations in sediment are two to three orders of magnitude higher than silver concentrations in ambient waters.

Heavy metal pollution in the sediments of the Coeur d'Alene River delta in Northern Idaho was investigated by Maxfield _et al_. (1974). Mining and smelting operations have discharged large quantities of wastes containing high levels of heavy metals in the river for several decades. Silver concentrations in the top layer of the dry sediments ranged from 6 mg/kg to 15 mg/kg, with a mean value of ± 2 mg/kg.

In the Southern California Coastal Zone, sediment samples were collected in four inner basins: San Pedro, Santa Monica, Santa Barbara and Soledad (Bruland _et al_. 1974). Silver appeared to have accumulated at higher rates in the San Pedro and Santa Monica basins and less distinctly in deposits at the Santa Barbara basin. This difference was attributed to human activities. In the Soledad basin, an area not measurably affected by human activities, concentrations did not change as a function of depth. Over 3 years, silver concentrations in sediment for both the San Pedro and Santa Monica basin increased from 1 mg/kg to 3.5 mg/kg and from 1 mg/kg to 3 mg/kg respectively. In the Santa Barbara basin, silver concentrations increased from 1 mg/kg to 2 mg/kg in sediment, and at the Soledad basin remained constant at a level of 2 mg/kg.

4. Dissolved and Suspended Matter

Water samples for 10 rivers across the United States were analyzed by Kharkar _et al_. (1968) to determine stream supply of several dissolved metals to the oceans. The concentration of silver was found to have a relatively narrow range among the rivers studied. Table 33 shows mean values of silver concentrations for the 10 rivers, ranging from 0.10 ug/l to 0.55 ug/l. These results are consistent with reports of

TABLE 32. SILVER CONCENTRATIONS DETECTED IN SEDIMENT, STORET 1977-1979

Major River Basins	No. Observations	Concentrations (mg/kg) Maximum	Mean
1. Northeast	14	10	10
2. North Atlantic	4	10	3
5. Ohio River	7	10	10
7. Upper Mississippi	3	1	1
9. Missouri River	10	2	1
10. Lower Mississippi	5	3	1
11. Colorado River	13	15	3
12. Western Gulf	92	22	2
13. Pacific Northwest	37	95	5
UNITED STATES	185	95	3

Source: U.S. Environmental Protection Agency, STORET, 1980.

TABLE 33. MEAN SILVER CONCENTRATIONS OF TEN U.S. RIVERS[1]

River and State	Mean Silver Concentrations (ug/1)
Mississippi, Minnesota	0.24
Susquehanna, Pennsylvania	0.37
Mad, California	0.26
Klamath, California	0.55
Russian, California	0.10
Eel, California	0.17
Brazos, Texas	0.38
Housatonic, Connecticut	0.39
Connecticut, Connecticut	0.17
Neuse, North Carolina	0.37

[1] In dissolved form

Source: Kharkar *et al*.(1968).

silver concentrations in dissolved form from the STORET system as shown previously in Table 29. For the nation as a whole, a mean value of 0.87 ug/l depicts silver concentrations in dissolved form for 1977 to 1979.

Turekian and Scott (1967) studied concentrations of silver in suspended material in 18 rivers in the eastern and southern portions of the country. They concluded that regional differences in concentrations were due to the presence of a greater quantity of a trace-element rich soil component and to industrial contamination in the eastern rivers. The Susquehanna River in Pennsylvania, in particular, was highlighted as the waterway stressing the regional variation due to the two factors mentioned. Results from the study indicate a range of 0.4 mg/l to 15 mg/l for silver concentrations in suspended matter; concentrations for each river are displayed in Table 34.

Silver concentrations in suspended matter recorded in the STORET system (0.002 mg/l to 0.06 mg/l; Table 35) are lower than those found by Turekian and Scott. Over the 10-year span between the Turekian and Scott (1967) study and the 1977 to 1979 values in STORET, the decreases in concentrations were parallel to those noted in the STORET ambient water concentrations.

5. Effluent Waters

The Interstate Sanitation Commission, which oversees the estuarine tidal waters of New York, New Jersey and Connecticut, examined heavy metals in wastewater and treatment plant effluents. Of 192 samples collected, less than 2% of the influent and less than 1% of the effluents contained silver concentrations above the detection limit of 50 ug/l (Mytelka et al. 1973).

In upstate New York, the Genesse River has received photoprocessing effluents for roughly seven decades. Sampling from May 31 to October 17, 1973, revealed an average silver concentration of 20 ug/l, although concentrations as high as 260 ug/l were recorded during the study period. The raw water intake at the main photoprocessing company in the area was documented as containing 1 ug/l of silver (Bard et al., 1976).

Page (1974) reported silver concentrations treated wastewater effluent in California averaging 7.1 ug/l, approximately 60% lower than the influent concentrations. In another study of California sewage treatment plant (Young et al. 1973), effluent silver concentrations were recorded as ranging from 2 to 20 ug/l.

Effluent silver concentrations in the STORET system are documented for three basins since 1977--Northeast, North Atlantic and Southeast. Summary maximum and mean effluents concentrations are:

TABLE 34. SILVER CONCENTRATIONS IN SUSPENDED MATTER IN U.S. RIVERS

River and State	Silver Concentrations (mg/l)
Brazos, Texas	0.4
Colorado, Texas	0.6
Red, Louisiana	0.3
Mississippi, Arkansas	0.7
Tombigbee, Alabama	1.0
Alabama, Alabama	4.0
Chattahoochie, Georgia	7.0
Flint, Georgia	1.0
Savannah, South Carolina	2.0
Klateree, South Carolina	1.5
Pee Dee, South Carolina	0.4
Cape Fear, North Carolina	0.7
Neuse, North Carolina	4.0
Roanoke, North Carolina	4.9
James, Virginia	7.0
Rappahannock, Virginia	1.0
Potomac, Virginia	1.5
Susquehanna, Pennsylvania	15.0

Source: Turekian and Scott (1967).

TABLE 35. SILVER CONCENTRATIONS IN DISSOLVED FORM AND ADSORBED ONTO MATTER IN MAJOR U.S. RIVER BASINS, 1977-1979

Major River Basins	Dissolved Form (ug/l)			On Suspended Matter (ug/l)		
	No. Obs.	Max	Mean	No. Obs.	Max	Mean
1. Northeast	253	2	.02	245	3	.14
2. North Atlantic	107	3	.05	85	2	.05
3. Southeast	462	3	.06	446	10	.14
4. Tennessee River	43	2	.14	41	2	.10
5. Ohio River	235	16	.14	224	3	.18
6. Lake Erie	67	1	.03	66	5	.12
7. Upper Mississippi	306	5	.20	268	10	1.39
8. Lake Michigan	69	1	.03	67	1	.09
9. Missouri River	440	50	.45	396	10	.72
10. Lower Mississippi	528	10	.10	468	60	.60
11. Colorado River	234	5	.13	208	30	.98
12. Western Gulf	378	15	.06	290	30	.66
13. Pacific Northwest	683	4	.41	340	20	.93
14. California	209	4	.03	143	10	1.22
15. Great Basin	397	85	5.70	143	10	.79
21. Lake Huron	25	1	.04	24	1	.28
22. Lake Superior	39	4	.19	39	10	.57
UNITED STATES	4475	85	.87	3493	60	.60

Source: U.S. Environmental Protection Agency, STORET (1980)

Basin	Observations	Concentration (ug/l) Maximum	Mean
Northeast	229	120	4.8
North Atlantic	62	730	18.7
Southeast	12	27	10.3
All Basins	303	730	7.8

6. Air

Silver is generally found at very low concentration in the atmosphere (Table 36). The differences in levels between urban and rural areas also appear to be relatively insignificant: in a sparsely inhabited region of Nebraska, Struempler (1975) reported a silver concentration of .15 ng/m^3; in the non-industrial city of Washington, D.C., Trout (1975) reported a concentration of 1.1 ng/m^3, and Brar et al. (1970), in a study of heavily industrial Chicago, Illinois, reported an ambient level of only 4.3 ng/m^3. In a study of urban areas including Chicago, Bogen (1974) reported levels ranging from 1 mg/m^3 to 2.4 ng/m^3. Even lower levels, 0.05-0.2 ng/m^3, were reported for San Francisco by John et al. (1973). Andren et al. (1974) reported a level of 0.17 ng/m^3 in the vicinity of three coal-fired steam plants at Oak Ridge, Tennessee. Almost all of the reported data are in general agreement with these levels. Thus the effect of human activity on atmospheric silver levels is limited.

Monitoring data for Europe reveal silver concentrations within this same range. In Glasgow, a heavily and diversely industrialized city, McDonald and Duncan (1979) reported levels ranging from 0.3 mg/m^3 to 12.9 ng/m^3, with a mean of 2.7 ng/m^3. Bogen (1974) reported a level of 4.2 ng/m^3 in Heidelberg, Germany.

In an examination of the contribution by steel mills to atmospheric levels of silver, Harrison et al. (1971) collected samples in the East Chicago area, located near three major steel mills, as well as other large manufacturing facilities. Silver concentrations ranged from less than 0.5 ng/m^3 to 5 ng/m^3.

When compared with iron levels at the same station, Dams et al. (1971) reported that since maximum levels of iron were not correlated with high silver levels, the steel plants were unlikely to be the source of the silver. The highest levels reported in the literature were measurements taken at the Kellog, Idaho, city hall; Ragaini et al. (1977) reported an average silver level of 10.5 ng/m^3, with a range of 0.94 ng/m^3 to 36.5 ng/m^3. The site is in close proximity to a smelting operation that processes lead with a high concentration of silver.

High levels may occur in areas of occupational exposure. Anania and Seta (1973) reported levels ranging from 0.01 mg/m^3 to 0.04 mg/m^3 (averaging 0.02 mg/m^3) at the San Francisco mint during melting and

TABLE 36. SILVER CONCENTRATIONS DETECTED IN AIR AND PRECIPITATION

Description	Concentration (ng/m^3) Mean	Concentration (ng/m^3) Range	Reference
Nebraska	0.15		Struempler (1975)
Washington, D.C.	1.1		Trout (1975)
Chicago, IL	4.3		Brar *et al*. (1970)
East Chicago, IL		1-2.4	Bogen (1974)
San Francisco, CA		.05-.2	John *et al*. (1973)
Oak Ridge, TN	0.17		Andren *et al*. (1974)
Glasgow, UK	2.7	0.3 -12.9	McDonald and Duncan (1979)
Heidelberg, Germany	4.2		Bogen (1974)
E. Chicago (steel mills)		0.5 -5	Harrison *et al*. (1971)
Kellog, Idaho (smelter)	10.5	0.94-36.5	Ragaini *et al*. (1977)
San Francisco Mint	.02mg/m^3		Anania and Seta (1973)
Cloud seeding	0.1		Standler and Vonnegut (1972)
	(ug/1)		
Nebraska - snow	0.05		Struempler (1975)
- rain	0.09		Struempler (1975)
St. Louis, Mo. - rain		0.002-.216	Rattonetti (1974)
Ag I - seeded precipitation		0.001-.45	Cooper and Jolly (1970)

casting operations. Similar levels may be present during production of medallions and other cast silver objects. Atmospheric levels during cloud seeding operations may also be significant. Standler and Vonnegut (1972) reported levels of approximately 0.1 ng/m^3 downwind of cloud-seeding operations.

Precipitation due to rain and snowfall is often a good indicator for levels of silver in the atmosphere and also aids in understanding the transfer of silver from air to water and the soil. In the previously mentioned study of uninhabited sections of Nebraska (Struempler 1975), a level of .08 ug/l was reported for silver in overall precipitation (0.05 ug/l for snow and 0.09 ug/l for rain). Rattonetti (1974) reported levels of 0.002-0.216 ug/l in St. Louis, Missouri in unseeded rainfall and Cooper and Jolly (1970) reported levels of 0.001 ug/l to 0.45 ug/l in AGI-seeded precipitation.

Mulvey (1979) examined precipitation, both snow and rain, in urban and uninhabited areas of the U.S. Uninhabited areas included Yellowstone National Park, the Sierra Nevada, and the Rocky Mountains in Colorado. For urban areas, he reported an average concentration of 36.9 ug/l and for uninhabited regions an average level of 27.3 ug/l.

7. Soil

The terrestrial concentration of silver has been estimated, on the basis of average concentrations in various rock formations, as between 0.02 mg/kg (Goldschmidt 1954) and 0.2 mg/kg (Green 1959) (Table 37). Taylor (1964) reported a concentration of silver in the continental crust of 0.07 mg/kg, based on 0.1 mg/kg in basalt and 0.04 mg/kg in granite. In comparison with these levels, concentrations of up to 7.0 mg/kg (Mitchell 1955) have been reported in mineral soils. High levels have also been found in forest humus, which appears to concentrate silver.

Boyle (1968) reported a similar range of from less than 0.01 mg/kg to 5 mg/kg in unpolluted soils, with an average value of .1 mg/kg. These average values are in close agreemtnt with concentrations found in various rock types, ranging from .04 mg/kg in granite to 0.12 mg/kg in gabbro (Boyle 1968). Though these are typical levels, silver-rich deposits can have concentrations reaching over 1000 mg/kg (Smith and Carson 1977).

In the humus of a birch forest, Vinogradov's (1959) soil samples indicated that humus can accumulate concentrations of silver much higher than levels in the underlying rock formation. He reported a level of 5.0 mg/kg. Mitchell (1955) reported generally lower levels than these in mineral soils, 0.1-1 mg/kg, but also reported a maximum of 7.0 mg/kg.

TABLE 37. SILVER CONCENTRATIONS DETECTED IN SOIL

Description	Concentration (mg/kg) Mean	 Range	Reference
Average rock formation	0.02		Smith and Carson (1977)
Average rock formation	0.2		Smith and Carson (1977)
Average rock formation	0.07		Taylor (1964)
Granite	0.04		Boyle (1968)
Gabbro	0.12		Boyle (1968)
Silver rich mineral deposits	>1000		Smith and Carson (1977)
Uncontaminated soil		0 .01-5	Boyle (1968)
Humus - Birch Forest	5.0		Vinogrado (1959)
Mineral Soils	0.1-1	max 7.0	Mitchell (1955)
Grand Rapids, Michigan			
Industrial	0.37		Klein (1972)
Agricultural	0.19		Klein (1972)
Residential	0.13		Klein (1972)
Airport	0.29		Klein (1972)
Lake Michigan - Power Plant -			
baseline	0.247		Klein and Russell (1973)
enriched	0.272		Klein and Russell (1973)
Fertilizer - super phosphate	30		Smith and Carson (1977)
phosphate rock		max 1000	Smith and Carson (1977)
Sludge - Ontario	25	16-44 (dry weight)	Fortescue _et_ _al_. (1975)
Municipal incinerator fly ash			
- Virginia	130		Law (1978)
- Washington, D.C.	190		Ruttermore _et_ _al_. (1972)
- Washington, D.C.	100		Wilson and Akers (1970)

Klein (1972) did a detailed study of silver in different urban land use areas of Grand Rapid, Michigan. The industrial classification included all land up to 1 mile beyond the land actually devoted to industrial use, agricultural land was soil used exclusively for agriculture, and residential land was primarily unimproved woodlands and low-density residential areas. Samples were taken from the top 2 in. of of the soil and at least 30 ft from any road. Industrial soils (0.37 mg/kg contained levels twice those of the agricultural areas (0.19 mg/kg) and three times the levels found in residential areas (0.13 mg/kg). Airport levels (0.29 mg/kg) fell between the industrial and agricultural levels. Elevated levels in the agricultural soils may in part be the result of the silver content in fertilizers, which typically ranges from a trace amount (30 mg/kg in super phosphate) to as high as 1000 mg/kg in phosphate rock (Smith and Carson 1977).

Sludge from waste treatment plants is often used for landfill or soil amendment. The silver content of sludge collected from the Niagara Peninsula of Ontario sewage treatment plants ranged from 16 mg/kg to 44 mg/kg, with an average value of 25 mg/kg (dry weight) (Fortescue _et al_. 1975). Law (1978) examined silver content in municipal incinerator fly ash destined for a landfill in Alexandria, Virginia. He reported a level of 130 mg/kg, comparable to levels in Washington, D.C. fly ash of 190 mg/kg (Buttermore _et al_. 1972) and 100 mg/kg (Wilson and Akers 1970).

F. SUMMARY

1. Physical and Chemical Properties

Silver is characterized by the low aqueous solubility of most of its compounds, a low elemental vapor pressure, and few physico-chemical resemblances to other metals commonly found in the environment. The most prevalent oxidation state is Ag(I). Silver can serve as a catalyst for oxidation reactions involving other substances. Numerous silver compounds exist including halides, cyanides, hydroxide, carbonate, and sulfur-containing compounds. Most are relatively insoluble, with the exception of silver nitrate, chlorate and perchlorate. Environmental mobility of silver may be increased, however, by its propensity to form complexes, primarily halides, cyanides, amines, and thiosulfate. Organo-silver compounds derived from unsaturated hydrocarbons are also found in the environment.

2. Fate and Distribution in the Environment

The typical fate and distribution of silver following release to the environment can be characterized by one of four source-dependent pathways: atmospheric emissions (accounting for 6% of total man-made releases), land disposal of solid waste including mine tailings (77%), aquatic discharges to surface water (10%) and aquatic discharges to Publicly Owned Treatment Works (POTWs) (7%).

a. Atmosphere

Atmospheric emissions originate from smelting activities, inadvertent releases (fuel combustion, steel manufacturing, etc.), and certain silver-consuming industries. Particles of less than 20 um diameter (from smelting and combustion) will be widely dispersed in the atmosphere in the form of oxides, sulphides, sulphates and chlorides, eventually reaching land and water via rainout and dry deposition. Particulates larger than 20 um in diameter (from smelters) are likely to settle out within 1 km of the source of emission. The form of silver in these particulates is expected to be the same as in the ore undergoing smelting.

Low levels of silver are commonly present in air in both urban and rural regions, generally at less than 5 ng/m^3. Levels are not notably higher than ambient levels in the vicinity of potential silver sources such as coal-fired steam plants or mills and smelters. Relatively high levels of up to 36.5 ng/m were detected near a smelter processing lead known to contain high silver concentrations. Weather modification activities do not appear to increase air silver levels much above levels in unseeded air.

b. Land

Land disposal of silver occurs in the form of spent tailings, coal pile stocks and municipal waste including solid waste from certain silver-consuming industries. Acid mine drainage does not appear to be an important contributor of silver releases. Once in the soil, the element is relatively immobile, with little potential for leaching into ground water. Because silver accumulates in the upper soil layer following soil surface application or disposal, it may be transported to water through runoff erosion.

Silver concentrations in soil are most commonly derived from parent rock rather than cultural sources. Typical ambient levels reflect the substrate concentration and thus are variable, ranging from 0.02 mg/kg to as high as 1000 mg/kg. An average natural background level is approximately 0.1 mg/kg to 0.2 mg/kg. Silver in sludge or other wastes being disposed of on land is at concentrations as high as 900 mg/kg, although a more typical level is 100 mg/kg; no information was available on levels at landfill sites following incorporation of the waste.

Little information was available on tissue levels of silver in terrestrial animals; the highest level reported was 2.0 mg/kg in ducks. In higher organisms concentrations are expected to be low due to the low efficiency of gastrointestinal absorption.

Background concentrations of silver in terrestrial plants ranged from 0.02 mg/kg in alfalfa tops to 5.5 mg/kg in mushroom caps. Experimental data indicate that silver may be accumulated at concentrations as high as 1,760 mg/kg in bush beans exposed to 10^{-5} M $AgNO_3$ for 13 days. In most cases, however, accumulation is not so extreme. Specific food crops with reported silver residues include whole wheat (0.4 mg/kg), wheat germ (0.8 mg/kg), tea (2 mg/kg), and fruits and nuts (up to 1 mg/kg).

Although data on accumulation of silver in terrestrial organisms are limited, silver does not appear to have a strong potential for biomagnification in terrestrial food chains.

c. Water

Aquatic discharge of silver is practiced by the photographic industry, both in production and development, by smelters and by electroplaters at low levels. Most companies practice in-house recovery techniques, using precipitation, ion exchange, electrolytic recovery, and/or reductive exchange. Fifty percent of the photographic producers discharge to POTWs. Amateur photographers discharge untreated wastes, primarily to POTWs; however, the total amount is small. In surface water, the fate of the discharged silver is dependent on its form. Thiosulfate silver complexes, which are the primary form released by the photographic industry, are degraded slowly and then precipitated as a halide or sulfide. The distribution of silver ions between the ionic form and complexes is dependent upon pH, redox potential, and the concentration of complexing agents present. According to the results of a chemical speciation model, $AgCl_2^-$ is the most prominent form in marine waters, with only negligible amounts of the ionic form. In freshwater in the presence of sulfur, AgHS predominates, especially in areas of low salt concentrations. In freshwater streams, approximately 10% of the total load of silver is found in suspended sediment. In the vicinity of sources, silver is accumulated in the bottom sediment, expecially in the surface layer.

Monitoring data for total silver levels in surface water indicate typical annual mean concentrations of less than 10 ug/l for individual river basins and nationally. Regions with higher than average concentrations include the North Atlantic, South Atlantic, and North Mississippi River basins. Silver concentrations in well water averaged 14 ug/l, with a high of 30 ug/l. Samples from mining areas revealed concentrations even lower than the national average.

Sediment levels of silver in surface water usually range from 1 mg/kg to 10 mg/kg, with a high of 95 mg/kg; sediment concentrations are usually two to three orders of magnitude above water levels. In suspended matter in rivers, silver concentrations ranged usually from 0.4 ug/l to 15 mg/l in 1967; more recent data indicate that levels were usually less than 0.06 mg/l. Levels to surface waters in effluent industrial wastewater, and sewage treatment discharges are generally less than 20 ug/l (mean values), with a maximum of 730 ug/l.

Most laboratory studies of the accumulation of silver by aquatic biota are for freshwater fish. However, some data are available on the levels of silver present in samples of marine species as well as the levels detected in the same species from polluted versus unpolluted sites.

The internal organs of largemouth bass are reported to accumulate 0.6 mg/kg silver, whereas the bone of cut-throat trout contained up to 4.4 mg/kg silver. The mean concentration of silver in fish from U.S. river basins according to STORET is 0.235 mg/kg, with a range of 0.004 to 1.9 mg/kg. Other studies report levels up to 9 mg/kg (in shellfish). In general, however, concentrations rarely exceed 1.0 mg/kg in marine and freshwater fish and invertebrates. Reported bioconcentration factors (tissue levels/water levels) range from 2.4 to 333 for various freshwater fish species. Marine species have a greater tendency to accumulate silver, and have been reported to accumulate silver to levels that are 3300 times the concentration in surrounding seawater. (Oyster gills from a polluted site contained 189 mg/kg silver.)

Silver residues of 0.01-0.48 mg/kg have been reported for vascular marine plants, while 0.2-0.8 mg/kg has been reported for algae species. Freshwater plants have been reported to contain up to 0.026 mg/kg silver. Both marine and freshwater plants have been reported to concentrate silver by factors of up to 200.

Bacteria were reported to accumulate 182,000 mg/kg silver from solution. The environmental parameters affecting the bioaccumulation of silver include temperature, oxygen concentration, pH, water hardness, the presence or absence of other cations, and soil organic matter content.

Aquatic organisms have a greater potential for bioaccumulation of silver than terrestrial organisms due to a greater potential for exposure. However, due to the generally low rates of absorption in most species, bioaccumulation is not expected to be significant. Seaducks, a species at a high level in the aquatic food chain, were observed to accumulate silver to levels one order of magnitude greater than the level in their food.

d. POTWs

In POTWs treatment techniques such as lime and settling, activated carbon, and cation-exchange are over 90% effective in removing silver from influents. In most POTWs, however, the latter two techniques are not used. In facilities utilizing more conventional technology, 75% of the silver is partitioned into the sludge at concentrations on the order of 100 mg/kg or greater. These levels are not expected to affect microbial activity in activated sludge.

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CHAPTER V.

EXPOSURE AND EFFECTS--BIOTA

A. EXPOSURE OF BIOTA

1. Introduction

Fish and wildlife are exposed to low-level natural background concentrations of silver present in environmental media, as well as to higher concentrations near anthropogenic sources of silver. A major portion of the total silver discharge is to land (79%) (Chapter III). Although the amount released to water and POTW's is low (17%), there is always potential for transfer of silver between soil and water through sediment transport, in addition to accidental discharges to water due to spills or leaks. The following section discusses the potential for exposure of aquatic organisms, terrestrial plants, and microbial systems to silver, both in general and in the vicinity of specific sources of silver releases.

To understand the contribution of human activity to silver exposure levels in soil and water, it is important to account for the natural background levels of the metal in these media. Silver is present in different types of parent material at low concentrations, approximately 0.05 mg/kg to 0.7 mg/kg (Lisk 1972). Typical soil levels vary between 0.1 mg/kg and 100 mg/kg, depending on local site characteristics (e.g. composition of parent material, source of organic matter, degree of weakening). In freshwater, silver levels vary from non-detectable to 38 ug/l with an estimated average of 0.24 ug/l (Boyle 1968). Background levels are discussed in greater detail in Section IV-B. Although a considerable degree of variability exists in soil and water background levels, few studies of anthropogenic silver contamination make a point of estimating and subtracting the background levels from the total measured level. As a result, an overestimation of industrial or other anthropogenic contributions of silver to a specific location may occur.

The following discussion is divided into exposure categories relating to mode of exposure and specific silver sources:

(1) Surface water - exposure of aquatic systems;

(2) Exposure due to weather modification activity;

(3) Exposure due to land disposal of solid waste containing silver; and

(4) Exposure of waste water treatment populations.

Since releases of silver to the atmosphere are less than 5% of total discharges, the exposure of biota to silver in air is expected to be minimal and has not been considered.

2. Aquatic Systems Exposed to Surface Water

a. Exposure Levels - Monitoring Data

Between 1970 and 1979, the mean concentration of silver in 15,610 observations regarding surface water in all major river basins ranged from 1.0 ug/l to 9.0 ug/l (Chapter IV.E). The variation in mean concentrations among river basins is low; the major river basins with the highest levels were the Northeast, California, Western Gulf, and the Ohio River and Tennessee River. Only for the Northeast basin were high concentrations (>0.05 mg/l) reported for more than 1 year. Concentrations decreased between 1970 and 1979 in most river basins; the exceptions were the North Atlantic, Southeast, and Lower Mississippi basins. Even with increases in levels of silver, the annual mean concentrations in these basins did not exceed 0.05 mg/l.

Another method of interpreting the STORET data considers what percentage of the total number of observations fall within the various segments of the entire range in measured concentrations. Tables 29-30 (in Chapter IV-e) present these data for the years 1970-1979 for the entire U.S. and for each major river basin. For the years 1975-1979 and all river basins, 59% of all concentrations observed were ≤ 0.10 ug/l, 10% ranged from 0.11 ug/l to 1.0 ug/l. 20% were between 1.1 ug/l and 10 ug/l, and 11% were greater than 10.1 ug/l (Table 38). Individual river basins in which the distribution of observations was weighted toward the high end of the concentration range were the Southeast, Ohio River, Lake Erie, California and the Western Gulf Basins.

b. Sources of Silver Releases to Surface Waters

According to the materials balance data (Chapter III), the photographic industry (photo equipment producers, professional photoprocessors and amateur photographers) is responsible for the majority of the known annual aquatic discharge of silver. Each subcategory has its own characteristic discharge practices. For example, producers discharge comparable amounts of silver to both POTW's and surface water; photoprocessors and amateurs are expected to discharge primarily to POTW's.

Although other industries are responsible for minor releases in terms of the national mass balance of silver, small discharges can nevertheless be responsible for significant exposure levels on a local scale. For this reason, the contribution of selected industries to aquatic exposure is discussed in the following section. The relative importance of these sources can be better understood by examination of materials balance/effluent guidelines data, qualitative information on industrial processes, and field studies of local impact. Industries that discharge directly to POTW's are considered in a later section on exposure of wastewater treatment populations (V.A.5).

TABLE 38. DISTRIBUTION OF UNREMARKED OBSERVATIONS FOR SILVER CONCENTRATIONS IN MAJOR RIVER BASINS, 1975-1979 (ug/l)

Major River Basin	≤ 0.10	0.11-1	1.1-10	10.1-100	>100	Total
Northeast	321 (88)	29 (8)	8 (2)	7 (2)		365
North Atlantic	594 (65)	102 (11)	125 (14)	96 (10)	2	919
Southeast	492 (78)	54 (9)	12 (2)	76 (12)		634
Tennessee River	70 (42)	61 (37)	22 (13)	14 (8)		167
Ohio River	491 (35)	70 (5)	447 (32)	404 (29)	4	1416
Lake Erie	135 (36)	6 (2)	29 (8)	206 (55)		376
Upper Mississippi River	633 (89)	38 (5)	34 (5)	6 (1)	3	714
Lake Michigan	137 (71)	34 (18)	19 (10)	2 (1)		192
Missouri River	1308 (68)	331 (17)	245 (13)	38 (2)		1922
S. Central Lower Mississippi River	767 (34)	278 (12)	1081 (48)	133 (6)	6	2265
Colorado River	983 (84)	64 (5)	94 (8)	28 (2)	2	1171
Western Gulf	360 (68)	44 (8)	63 (12)	64 (12)	2	533
Pacific Northwest	371 (73)	70 (14)	57 (11)	7 (1)		505
California	137 (46)	21 (7)	92 (31)	46 (15)	3 (1)	299
Great Basin	228 (60)	26 (7)	89 (23)	25 (7)	12 (3)	380
Lake Huron	27 (45)	6 (10)	27 (45)			60
Lake Superior	37 (76)	6 (12)	5 (10)	1 (2)		49
TOTAL	7091	1240	2449	1153	34	11967
Percentage of Total	59	10	20	10	1	

Source: STORET Water Quality Control Information System.

i. Photography

According to the Materials Balance (Chapter III), approximately 50 kkg of silver is discharged directly to surface water by producers of photographic equipment. Other categories are assumed to discharge primarily to POTW's. The discharge estimate is based on raw wastewater concentrations assuming no treatment. The highest concentration was for the silver halide subcategory with a mean of 14 mg/l and a maximum of 37 mg/l. The forms of silver released for all subcategories are either silver halide complexes or thiosulfates.

No field studies were available which concerned the impact of photographic discharge on aquatic systems. Therefore, the relationship between aquatic exposure and this industry is not well understood. Certain factors, however, are likely to reduce potential exposure levels. Since the recovery of silver is cost-effective for the photographic industry and effective recovery techniques are available (U.S. EPA 1980), it is expected that the raw wastewater levels would be reduced significantly before discharge in the plant effluent. Additionally, the forms discharged are relatively insoluble. The compounds, therefore, would either form complexes and/or end up in the sediment, reducing the biological availability of the silver (Chapter IV-C).

ii. Electroplating

Although electroplaters consume a relatively small amount of the silver produced each year (4,5%) and are responsible for minor aquatic discharged on a national level, the industry may have local impacts on aquatic systems, at least in terms of accumulation. No information was available on electroplaters who use silver; however, elevated concentrations of silver (up to 15.3 mg/kg dry weight) were reported in the surficial sediment in the vicinity of an electroplating facility located on a bay in Rhode Island (Eisler _et al_. 1977). Other metals such as chromium, copper, lead, and zinc were present at concentrations one or two orders of magnitude higher than silver levels. At the same site, following the plant's closure, samples of clam tissue were found to contain 1.16-4.64 mg/kg silver (dry weight), as well as other metals; all levels were significantly higher than those in control samples (Eisler _et al_. 1977) and indicated the presence of silver even after the discharge has ceased. If the availability of the form of silver is negligible at high salinity levels as indicated in the model of Jenne _et al_. (1980), then much of the silver release from electroplating operations would also not be available for uptake by aquatic species.

iii. Mining and Milling

In mining wastes, silver is found at concentrations one to two orders of magnitude below the concentrations of zinc, copper, cadmium, and other metals. This is at least partially explained by the fact that more effort is spent in recovering silver from these wastes due to economic incentives. Therefore, although silver is generally more toxic than most other metals, it is found in mining wastes in conjunction with relatively larger concentrations of other metals and thus is probably a minor contributor to the toxicologic characteristics of the wastes. Total discharges of silver to water from mining operations are expected to be negligible (<1 kkg) due to recovery practices and the low initial silver concentrations (Chapter III).

Most of the silver mining activity is concentrated in the Coeur D'Alene river basin in Idaho (River Basin No. 13). Unlike the data for copper, the STORET data base does not report higher than average silver concentrations for surface water in this river basin. In addition, the mean concentration of silver in this basin has decreased by nearly 100% between the 5-year periods 1970-1974 and 1975-1979 (Figure 16). This may be the result of averaging levels for areas of the basin in which no mining occurs or the low discharge rates associated with mining and milling. Aggregate data for a major river basin reveal only the most obvious overall trends in the distribution of pollutant concentrations.

In a risk assessment for copper (Perwak et al. 1980), more in-depth investigation of the Coeur D'Alene area revealed that the surface waters were relatively soft (<50 mg/l $CaCO_3$), the pH was between 5.0 and 7.0, and the concentration of complexing agents was expected to be low. The combined effect of these factors would favor the soluble form of all metals, including silver. Some areas of the basin, notably the South Fork, were obviously very toxic to aquatic life; however, the presence of extremely high concentrations of other metals (zinc at up to 5000 ug/l, cadmium at 25 ug/l, silver was not reported) would implicate these metals or the combined effects of all of the metals present as the cause of toxicity rather than the probably low levels of silver. Unfortunately, minor river basin data were not available to determine the silver concentrations at individual sampling stations.

In conclusion, an area of high mining activity with environmental characteristics conducive to metal toxicity was found to have localized areas with potentially toxic concentrations. Either seasonally (during periods of dilution) or for short-term exposures, these concentrations did not elicit toxic effects in aquatic basins. The concentrations of other metals, in the Coeur D'Alene basin and in all mining areas, are so great that the contribution of silver to the overall toxicity is expected to be overshadowed by and indistinguishable from the effects of other metals.

3. Weather Modification

Cloud seeding activity has decreased on a nationwide basis largely because of mixed results of early experiences. Issues associated with the practice include liability for "stealing" someone else's rain; liability for producing rain in areas that do not want it; and reduced availability of federal funding. Small applications by independent operators are continuing, but the scale is reduced from that of the Federal programs several years ago.

The recent sharp increases in the price of silver has made the use of silver in cloud-seeding operations less cost-effective than the available substitutes. Compared with other agents, the principal advantage of silver iodide is its ability to induce ice crystal formation at high temperatures. Because of its chemical properties, AgI can be finely subdivided; this enhances its ability to disperse, which increases potential for initiating crystallization. Several organic compounds (phioroglucinol, 1,5-dihydroxynaphthalene and metaldehyde) have been suggested as alternative cloud-seeding agents. They induce crystallization at higher temperatures than AgI but are not as efficiently dispersed from ground generators (Cooper and Jolly 1970). Several factors point to a decline in the use of silver iodide. Advances in weather modification indicate a greater reliance on pyrotechnic devices, aircraft, and other aerial delivery systems that do not require AgI, and less reliance on ground generators.

Thus, weather modification activity has decreased and the application of silver iodide is also declining. The danger of silver in this application is not expected to be sufficient to warrant significant concern for exposure of most natural populations. Microorganisms, however, are more likely to be affected than other species so that exposure levels resulting from weather modification warrant further consideration.

A three-year study of a large area in the San Juan Mountains undergoing weather modification reported no significant increases in silver levels in different media (Teller et al. 1976). It is often not possible to distinguish the silver resulting from modification from natural background levels (Klein 1978). The possibility of greater Ag accumulation in another habitat, however, cannot be discounted due to the number of variables which determine silver concentrations in soil.

A worst case example of silver effects resulting from weather modification activity is illustrated in a field study investigating the relationship between silver concentrations in the soil surrounding a cloud-seeding generator and its effects on microbial activity (Sokol and Klein 1975). Concentrations as high as 1400 ug/g soil (ash) were detected within 50 m of the generator, primarily in the top 2 cm of soil. An apparent decrease in organic matter turnover rate was associated with the high silver levels as well as a higher soil water content, lower pH, higher respiration rates (six times greater than the control), and slightly higher microbial populations.

In conclusion, weather modification activities probably do not result in significant exposure levels for natural populations or microorganisms. Areas exposed to such high silver concentrations, such as near generators, are very few and, due to the immobility of silver in soil, are contained and have little likely impact on surrounding areas.

4. Land Disposal of Silver Waste

A major portion of all silver releases to the environment are made directly to land. Waste is applied in the form of industrial sludges from wastewater treatment, solid waste (in junked steel scrap, home appliances) and in sludges from POTW's. An estimated 370-520 kkg silver is applied to landfill in solid form each year, with up to 220 kkg in POTW sludge. Other sources of silver to land include leaching of tailings ponds, spills from tailings ponds, and industrial waste holding lagoons (Smith and Carson 1977); however, the amounts released from these sources are expected to be small.

The type of silver product or the chemical form released to the environment will determine its mobility. Silver in solid wastes is inert and virtually immobile. The behavior of silver in sludge applied to a disposal site depends on sludge and site characteristics. Most forms of silver are insoluble salts (chlorides, hydrous oxides, halides), which would be immobilized by precipitation. In the presence of organic matter, complexation and/or adsorption will occur. In addition, the inorganic fraction of the soil will also readily adsorb silver. Certain site characteristics (e.g., sandy, low organic soils, low pH, immediate proximity of water table) may support movement of silver out of a containment area, but these opportunities are expected to be few. In general, silver remains on the top 2 cm of soil. Certain disposal practices (e.g., in a liquid form into a holding lagoon) have a higher potential for releasing silver from the disposal site, especially if the metal is suspended or dissolved in liquid. Again, however, following a spill, the surrounding soil would be expected to retain the metal and it is unlikely it would move into ground water or nearby surface water.

Several activities may lead to high silver exposure levels in soil. Weather modification activities, as described previously, are a potential source of higher than background levels of silver in soil although the induced concentrations appear to be low. Land application of sludge from wastewater treatment facilities may expose microbial populations to high silver levels in soil. Sludge contains silver at levels as high as 900 mg/kg, although more commonly at 100 mg/kg (Smith and Carson 1977); however, these levels are approximately an order of magnitude below the soil concentrations surrounding the cloud-seeding apparatus and would be further diluted by incorporation into soil before exposure of microbial populations. Much of the silver present in sludge is apparently recovered and recycled before the material is disposed of on land. In addition, disposal is usually limited to controlled waste disposal sites where there would be little potential for interference with natural microbial processes. Other reported soil concentrations, either background levels or those near indirect sources (Chapter IV-E), are significantly lower than the levels reported previously, averaging 0.37 mg/kg in industrial areas and 0.19 mg/kg in agricultural areas. No information was available on silver levels in mining areas.

In conclusion, it appears unlikely that silver in soil will reach significant levels except in the immediate vicinity of a silver source. Under conditions of continual release, significant levels may accumulate due to silver's immobility (Chapter IV-C). At this time, however, no such situation is known.

5. Sources of Silver to Wastewater Treatment Systems

There has been speculation that silver may interfere with microbial processes in wastewater treatment due to its known microbiocidal effects at low concentrations. Typical ambient concentrations of silver in surface waters are lower than those triggering effects (Chapter IV-C);

however, in the vicinity of certain sources, discharges of silver at high concentrations and/or on a continuous basis could affect sewage treatment processes. -

Amost all amateur photographers, photoprocessors, and certain photographic equipment producers discharge their effluents directly to POTW's. Silver is usually released in the form of halide complexes or thiosulfate which would partition into the sludge (Chapter IV-C). Concentrations of up to 5 mg/l in photoprocessing water were followed through wastewater treatment and found to have no adverse effect on biological activity (Bard et al. 1976). Typical concentrations of silver in photoprocessing effluents are expected to be lower; for example, 0.28 mg AgI was detected in a sewage influent originating from a process plant (Bard et al. 1976). Home photographers for the most part do not practice silver recovery for their wastewater. Ag concentrations are on the order of 12g/1 in raw waste, but the waste is diluted when poured down the sink (see Section III). Home photographers are widely distributed and discharge intermittently a total annual release of approximately 15 kkg. They are thus expected to have a minimal impact on microbial processes on a national scale. No information was available on POTW influent concentrations from other dischargers.

B. EFFECTS ON BIOTA

1. Introduction

Before low doses of silver can be toxic to biota, the ionic form of the metal must come into direct contact with metabolically active sites, such as cell membranes of microorganisms or the gas exchange surfaces of fish gills. The solubility of many silver salts is low making these compounds less accessible for biological uptake. $AgNO_3$ is quite soluble and therefore is commonly used in laboratory studies. Silver is generally considered to be more toxic to aquatic life than mercury (Phillips and Russo 1978).

In studies of the pollutants to aquatic organisms, a certain amount of inconsistency in bioassay results may be expected, owing to several factors. Static toxicity tests are designed to simulate the aquatic environment of a standing or slowly flowing body of water that has received a single discharge of toxicant. In a continuous-flow bioassay, toxicant concentrations are maintained by repeated addition of the toxic substance, thus simulating a constant, chronic exposure such as might be found near an industrial site. In both types of experiments, the toxicant concentrations are often determined nominally (i.e., by diluting a measured amount of the substance), and may not be directly monitored during the test. Nominal determination of silver concentrations does not account for absorption and metabolism by test organisms, absorption onto particles and test tank walls, or for complex formation when complexing agents are present, and so may result in less accurate estimations of lethal and sublethal levels. Consequently, a wide discrepancies may appear between the results of a static nominal bioassay and those of a continuous-flow test in which the toxicant concentrations were measured during the exposure period.

2. Freshwater Organisms

a. Acute Toxicity

Table 39 summarizes selected data on the acute effects of various concentrations of silver on freshwater vertebrate species. The values lethal to 50% of the test population (LC_{50}'s) depend upon the species and the particular conditions of the laboratory experiment (e.g., water hardness and temperature). The mean 96-hour LC_{50} of silver for rainbow trout was 6.5 ug/l and 13.0 ug/l in soft and hard water, respectively (Davies *et al*. 1978). Rainbow trout are considered to be one of the species of fish most sensitive to heavy metals (Davies 1975). The range of silver concentrations observed to cause mortality was from 4.3 ug/l (guppies) to 100 ug/l (sticklebacks).

Silver is believed to interfere with gas exchange in the gills of fish, but the mechanism is not understood. Some investigators suggest that silver in a dilute solution causes secretions of mucus in the gill, filling the interlamellar spaces to the point that normal movement of the gill filaments becomes impossible. Since this prevents the contact between water and gill tissues that is necessary for oxygen uptake, the fish die of suffocation. Other investigators believe that the mode of action involves the swelling and breakdown of gill epithelium, perhaps through the blocking of enzymes. Because low Ag concentrations often are lethal to fish, the second hypothesis is thought to be more likely.

Table 40 summarizes data concerning the acute effects of silver on other freshwater species. Concentrations as low as 1.5 ug/l have acute effects on *Daphnia magna*. A concentration of 6.0 ug/l was reported to kill *Escherichia coli* in 2-24 hours (Cooper and Jolly 1970).

b. Chronic and Sublethal Toxicity

Table 41 summarizes the chronic and sublethal effects of silver on freshwater vertebrates. The chronic "no effects" concentration for silver was determined to be between 0.09 ug/l and 0.17 ug/l based on 18 months' exposure in soft water. This concentration defines the level exerting no obvious effect, but does not account for possible reductions in spawning behavior or reproduction because the study was terminated before the female rainbow trout reached sexual maturity of 3 years. Silver concentrations of 0.17 ug/l or greater reduced egg hatching success and the growth rate in fry (Davies *et al*. 1978).

Coleman and Cearley (1974) found that the rate of weight gain of blue gill and large-mouth bass exposed to silver decreased slightly (not significantly) as the concentration increased. These authors mentioned

TABLE 39. ACUTE EFFECTS OF SILVER ON FRESHWATER VERTEBRATES

Silver Concentration (ug/1)	Species	Effect	Water Hardness (mg/1 $CaCO_3$)	Reference
4.3	Guppy (*Poecilia reticulata*)	LC_{50}	-	Smith and Carson (1977)
6.5	Rainbow trout (*Salmo gairdneri*)	LC_{50} (96 hours)	Flow through, soft water (26)	Davies (1978)
10	Stickleback (*Gasterosteua aculeatus*)	Death in 96 hours	pH 6-6.8, very soft water (1)	Jones (1964)
13	Rainbow trout (*Salmo gairdneri*)	LC_{50} (96 hours)	Flow through, hard water (350)	Davies (1978)
28.8	Rainbow trout 2 months old	LC_{50} (96 hours)	Flow through, tested 5-80 ug/1	Hale (1977)
25	Chinook salmon fry (*Oncorhynchus tshawytscha*)	Majority killed in 48 hours	Tap water	Marsh and Robinson (1980)
64	Fathead minnow (*Pimephales promelas*)	60% mortality in 96 hours	Soft water (49)	Terharr *et al*. (1972)
70	Bass (no species given)	Death in 24 hours	Moderately hard (180)	Coleman and Cearley (1974)
100	Stickleback (*Gasterosteus aculeatus*)	Death in 24 hours	15-18°C, soft water (1)	Doudoroff and Katz (1953)

TABLE 40. ACUTE EFFECTS OF SILVER ON FRESHWATER INVERTEBRATES

Ag Concentration (ug/l)	Species	Conditions	Effects	Reference
.001-500	Bacteria		Bacteria killed (water sterilized)	U.S. EPA (1979)
1.5	*Daphnia magna* Cladoceran	Static soft water (40 mg $CaCO_3$/l)	LC_{50} (48 hours)	U.S. EPA (1979)
15.0	*Polycelis nigra* flatworm	4 days at 23-27°C	Death	McKee (1963)
30.	*Daphnia magna*	4 days a5 23-27°C	Death threshold toxicity concentration	McKee and Wolf (1963)
30.	*Microregma*	4 days at 23-27°C	Death	McKee and Wolf (1963)
1000	Water-snail *Australorbis Glabratus*	In distilled water	Fatal in 24 hours	Harry and Aldrich (1958)
1400	*Philodina acuticornis* Rotifer	Static	96-hour LC_{50}	Buikema *et al*. (1974)

TABLE 41. CHRONIC AND SUBLETHAL EFFECTS OF SILVER ON FRESHWATER FISH

Ag Concentration (ug/l)	Species	Compound	Conditions	Effects	Reference
0.09	Rainbow trout (*Salmo gairdneri*)	Silver nitrate $AgNO_3$	18 months: soft water	No mortality due to silver	Davies *et al*. (1978)
0.07-.13	Rainbow trout	AgI	1 year	No effects	Davies (1975)
0.17	Rainbow trout (*Salmo gairdneri*)	Silver nitrate $AgNO_3$	18 months: soft water	17.2% more mortality than control	Davies *et al*. (1978)
>0.17	Rainbow trout (*Salmo gairdneri*)	Silver nitrate $AgNO_3$	18 months: soft water 28 mg $CaCO_3$/l	Premature hatching of eggs; Reduced growth rate in fry	Davies *et al*. (1977)
0.2-0.8	Rainbow trout (embryo-larval)	Silver	Static: 28 days (fertilization to posthatching). Hard water (195 mg $CaCO_3$/l)	Threshold value (LC_1)	Birge *et al*. (1979)
0.6	Goldfish (embryo-larval) (*Carassius auratus*)	Silver	7 days (fertilization to posthatching. Hard water (195 mg $CaCO_3$/l)	Threshold value (LC_1)	Birge *et al*. (1979)
0.88	Rainbow trout (*Salmo gairdneri*)	AgI	6 weeks: soft water. 15 mg $CaCO_3$/l pH 6.5-6.8	94% of fish died, delayed fry swim-up by 2 weeks, retarded growth	Davies (1975)
3	Stickleback (*Gasterosteus aculeatus*)	Silver nitrate	large fish, soft water	Lethal concentration limit: survival time equals that of control (10 days)	Davies *et al*. (1978)
4	Stickleback	Silver nitrate	7 days: soft water (1 mg Ca)	Death of fish	Duodoroff and Katz (1953)

TABLE 41. CHRONIC AND SUBLETHAL EFFECTS OF SILVER ON FRESHWATER FISH (Continued)

Ag Concentration (ug/l)	Species	Compound	Conditions	Effects	Reference
10	Rainbow trout (embryo-larval stages)	Silver	28 days, hard water	LC_{50}	Birge *et al*. (1979)
30	Goldfish (embryo-larval stages)	Silver	7 days, hard water	LC_{50}	Birge *et al*. (1979)
70	Bluegill (*Lepomis macrochirus*)	Silver nitrate	6 months, hard water	No lethal effect	Coleman and Cearley (1974)

that metal concentrations having little or no effect on growth could be deleterious to other physiological functions later in the life cycle. Bass were reportedly more sensitive to silver than bluegill (Coleman and Cearley 1974). Adult oysters and fish are more resistant than other age classes; e.g., gametes, embryos, and fry (Smith and Carson 1977).

Table 42 summarizes chronic and sublethal effects of silver on freshwater invertebrates and other species. A concentration of less than 1 ug/l silver represents a 14-day $LC_{50}$for mayflies. Daphnia exposed to 5.1 ug/l silver in Lake Erie Water at 25°C were immobilized (Cooper and Jolly 1980). Other species were more resistant to silver.

Table 43 presents the effects of silver on freshwater algae. These species are generally not as sensitive as bacterial species. Concentrations of 10-140 ug/l retarded growth and 2000 ug/l was toxic in the species studied.

3. Marine Organisms

a. Acute Toxicity

No information was available on the acute effects of silver for marine vertebrates. Table 44 summarizes data on the acute effects of silver for marine invertebrates. The observed LC_{50}'s ranged from 3.7 ug/l for American oyster to 262 ug/l for mysid shrimp.

b. Chronic and Sublethal Effects

No information was available on the chronic and sublethal effects of silver on marine vertebrates. Table 45 summarizes data concerning the chronic and sublethal effects of silver on marine invertebrates. Observations of abnormal egg development and spawning delays were reported for concentrations of 2-103 ug/l for echinoderms and shrimp.

Data on the effects of silver on marine algae were limited. A 96-hour EC_{50} (concentration at which effects are observed in 50% of test organisms) was reported for the algae Skeletonema costatum at 130 ug/l. The effect was growth inhibition, as reflected by a reduction in cell number (U.S. EPA 1979).

TABLE 42. CHRONIC AND SUBLETHAL EFFECTS OF SILVER ON OTHER FRESHWATER SPECIES

Ag Concentration (ug/l)	Species	Conditions	Effects	Reference
<1	Mayfly *Emphemerella grandis*	14 days, $CaCO_3$ 30-70 mg/l	LC_{50}	Nehring (1976)
10	Narrowmouth-toad embryo-larval	7days, hard water	LC_{50}	Birge *et al*. (1979)
50-100	Snail *Australorbis glabratus*	24 hours, distilled water	Distress syndrome. Snail unable to attach itself to substrate	Harry and Aldrich (1958)
5.1	*Daphnia magna*	Lake Erie H_2O at 25°C	Immobilized	McKee and Wolf (1963)
30	*Daphnia magna*	River Haval in Germany	Threshold toxicity level	Bringmann and Kuhn (1959)

TABLE 43. EFFECTS OF SILVER ON FRESHWATER MICROFLORA

Ag Concentration (ug/l)	Organism	Conditions	Effect	Reference
10-60	*Chlorella vulgaris*		Growth retardation	Hutchinson and Stokes (1975)
20	Algae (no species given)	Silver nitrate	Average survival time is 2 days	Doudoroff and Katz (1953)
80	*Phormidium inundatum*	Silver sulfate	Prevented growth	Smith and Carson (1977)
140	*Phormidium inundatum* (blue-green algae found in swimming pools)	Silver nitrate	Prevented growth	Fitzgerald (1967)
2,000	6 Algae species		Toxic	Gratteau (1970)

TABLE 44. ACUTE EFFECTS OF SILVER ON MARINE INVERTEBRATES

Ag Concentration (ug/l)	Organism	Conditions	Effects	Reference
0.5	Sea urchin *Arbacia lixula*	52-hour exposure	Reduced egg development significantly	U.S. EPA (1979)
3.0	American oyster *Crassostrea virginica*	Embryo: (this is background conc. in seawater)	LC_0 Failure to develop	Calabrese *et al*. (1973)
3.7	American oyster *Crassostrea virginica*	Embryo 48-hour static test (5.8 ppb $AgNO_3$)	LC_{50}	Calabrese *et al*. (1973)
6.4	American oyster *Crassostrea virginica*	Embryo 48-hour static test (10 ppb $AgNO_3$)	100% mortality	Calabrese *et al.* (1973)
21	Hardshell clam *Mercenaria mercenaria*	Embryo 48-hour static	100% mortality	Calabrese *et al*. (1973)
33	Bay scallop (juvenile) *Argopecten irradians*	Static	LC_{50}	Nelson (1976)
40	Killifish (mummichog) *Fundulus heteroclitus*	Ag^+ (Salt), 96 hours in 20-25°C. seawater	Inhibition of 3 liver enzymes (first step of toxicity or metabolic impairment)	Jackim and Hamlin (1970)
262	Mysid shrimp *Mysidopsis bahia*	Flow through 96 hours	LC_{50}	Sosnowski and Gentile (und.)

TABLE 45. CHRONIC AND SUBLETHAL EFFECTS OF SILVER ON MARINE INVERTEBRATES

Ag Concentration (ug/l)	Species	Compound	Conditions	Effects	Reference
2	Echinoderm (*Paracentrotus*)	$AgNO_3$	-	Delay in development and deformation of plutei	Davies *et al*. (1978)
10	Echinoderm (*Paracentrotus*)	$AgNO_3$	-	Inhibited and abnormal development of eggs	Soyer (1963)
10.2	Mysid shrimp (*Mysidopsia bahia*)	$AgNO_3$	58 days 20°C	No effect on growth, reproduction, or survival	U.S. EPA (1979)
3.3	Mysid shrimp (*Mysidopsia bahia*)	$AgNO_3$	58 days 20°C	Delay in spawing time, smaller brood size	U.S. EPA (1979)
103	Mysid shrimp (*Mysidopsia bahia*)	$AgNO_3$	58 days 20°C	No spawning	U.S. EPA (1979)

4. Factors Affecting Toxicity to Aquatic Species

Some of the parameters that affect aquatic toxicity include water hardness, temperature, concentration of dissolved oxygen, pH, form of the silver, other solids present, and fish size and species.

Silver toxicity has been observed to decrease with increases in water hardness. This is probably the result of increased anion complexation and precipitation of silver, which reduces the amount available for uptake (Davies et al. 1978). The effects of silver are also likely to be greater in pure water than in water that contains appreciable concentrations of other metal ions (Cooper and Jolly 1970). Silver is less toxic in hard, alkaline waters with pH from 7.5 to 9.5 than at lower pH's (Smith and Carson 1977).

Smaller fish may be more susceptible to injury from silver than are larger fish. This is most likely a consequence of greater respiratory and metabolic rates in smaller fish. Long-term exposure may increase the resistance of an aquatic organism to silver (Davies et al. 1978).

5. Terrestrial Organisms

a. Animals

Chronic exposure studies of birds and mammals have revealed effects of silver including lowered immunological activity, altered membrane permeability, vascular hypertension, enzyme inhibition, and shortening of life spans (Smith and Carson 1977).

Continued intake of silver or silver compounds by mammals may cause an irremediable discoloration of the skin and mucous membranes called argyria which does not in itself involve other serious effects (Cooper and Jolly 1970). Silver administered orally to mice has caused ovarian cytopathic effects (Hadek 1966) and in mammals, in general, may cause ventricular hypertrophy (Olcott 1948).

b. Plants

Table 46 summarizes the effects of silver on terrestrial plants. Silver is not considered likely to be concentrated to harmful levels through terrestrial food chains (Cooper and Jolly 1970). Many investigators consider silver to be one of the most toxic heavy metals to fungi, slime molds, and bacteria (Cooper and Jolly 1970).

Dilute solutions of silver nitrate have been toxic to wheat and pea seeds, while 20 mg/l has seriously injured tomato and snapdragon seedlings (Smith and Carson 1977). Metallic silver has been noted to stimulate root growth of watercress, onion and other plants while it inhibits root growth of tobacco (Smith and Carson 1977). Silver is more phytotoxic in soils low in organic matter than in soils with high levels (Romney et al. 1977). Exposure of germinated Pisum seeds to a

TABLE 46. EFFECTS OF SILVER ON TERRESTRIAL PLANTS

Ag Concentration in solution (ug/1)	Species	Effects	Reference
4900	Lupine	Fatal	Clark (1899)
9800	Maize	Fatal	Clark (1899)
20,000	Wheat and Pea (seeds)	Toxic	Smith and Carson (1977)

TABLE 47. EFFECTS OF SILVER ON MICROORGANISMS

Ag Concentration (ug/1)	Species	Effects	Reference
1-1200	Bacteria, yeast and fungi (in water substrate)	Death (in 2-24 hours)	Goetz *et al*. (1940)
6 ($AgNO_3$)	*Escherichia coli*	Death (in 2-24 hours)	Smith and Carson (1977)
35 (AgI)	*Escherichia coli*	Death (in 2-24 hours)	Smith and Carson (1977)
10	*Mycobacterium*	Completely inhibited growth	Golubovich (1974)
100[1]	*Arthrobacter* soil microorganism	Inhibited growth (and, therefore, retarded cellulose decomposition of mud by 10%)	Smith and Carson (1977)

[1] Unit is ug/g of mud.

solution with a 0.001 M concentration of silver ions caused chromosomal damage in the form of swollen prophase cells (U.S. EPA 1979, Von Rosen 1954).

Growth for 13 days in a 10^{-5} M solution of $AgNO_3$ reduced the yield of bush beans by 85% (from 1.4 g/plant to 0.21 g/plant) and decreased the calcium in the leaves by 67%. The result of decreased Ca uptake may be impaired membrane permeability, resulting in leakiness and increased phytotoxicity (Wallace and Romney 1977, Wallace 1979). Davis and Beckett (1978) determined a tentative toxicity threshold for accumulation of silver in young barley tissue. These authors suggested that accumulation of more than 4.0 ppm silver causes adverse effects on growth (Davis and Beckett 1978). (Table 28 in Chapter IV identifies background levels in terrestrial plants).

6. Microorganisms

Silver ion is highly toxic to microorganisms and has been used, especially in the past, as a microbiocide to sterilize water at concentrations of 0.001-500 ug/l (usually 0.5 ug/l) (Smith and Carson 1977, Cooper and Jolly 1970). In plate culture studies for more acute exposure, silver ion added as $AgNO_3$ inhibited microbial growth at 6 ug/l and when added as AgI did so at 35 ug/l (Sokol and Klein 1975). An anaerobic study of cellulose degradation in mud indicated a 10% decrease in rate from the control at 100 ug AgI/g (Sokol and Klein 1975). Table 47 summarizes these results of laboratory studies on silver toxicity to microorganisms.

Under more natural conditions in soil, silver iodide was found to reduce microbial activity while $AgNO_3$ did not under equivalent conditions. In a field study of silver accumulation and effects resulting from AgI applied to a grassland system (Klein and Molise 1975), threshold concentrations for decreased breakdown (of glucose) were measured at 1.0 to 2.0 ug silver/g ash (in soil) with a significant decrease at greater than 60 ug/g. No effects were observed below 0.6 ug/g. Equivalent tests on silver nitrate showed no effects at even the higher concentrations though it is a more water soluble compound than AgI. The authors attributed the greater toxicity of AgI to its interaction with ammonia, amines, and other compounds present in soil, substances which would increase its solubility.

Effects of silver iodide and silver phosphate on the usually more sensitive anaerobic and aerobic processes of wastewater treatment microbial populations were investigated (Castignetti and Klein 1979). Silver present at concentrations up to 236 ug/l in culture media had no significant effect on methanogenesis; in fact, stimulation was observed at lower concentrations (32-64 ug/l) of silver phosphate. Concentrations of 500 ug/g of silver in sewage sludge (as $AgI\text{-}NH_4$ and Ag-NaI) significantly reduced methanogenesis. A less common form of silver, $AgI-TiO_2$, was considerably more toxic, significantly reducing the process at 1.0 ug/g (Klein and Giangiordano 1976).

C. SUMMARY

Fish and wildlife are exposed to natural background levels of silver and also concentrations of cultural origin. The majority of surface water levels are less than 0.10 ug/l with approximately 30% between 0.11 ug/l and 100 ug/l and less than 1% greater than 100 ug/l. Major river basins with consistently higher concentrations include the Southeast, Ohio River, Lake Erie and Western Gulf. The Northeast also registered occasional individual incidents of high concentrations.

Intensive recovery practices are in effect in all large silver-consuming industries, due to economic incentives, and usually remove a large fraction of silver from raw wastewater before discharge. Most of the silver discharged is believed to either form complexes or to precipitate and settle into the sediment layer. Silver is present in mining and milling wastes in conjunction with other metals which occur at higher concentrations and thus tends to exhibit a greater toxicity than for silver alone.

Use of silver as a cloud-seeding agent does not appear to significantly increase silver concentrations in treated areas except in the immediate vicinity of generators. Soil microorganisms may be exposed to high silver levels in such locations.

Silver releases to land in most cases do not appear to be associated with high exposure levels for terrestrial organisms. Silver applied in sludge is expected to be immobilized in soil and contained at the site of disposal. Silver released in solid waste form (e.g. old appliances) is also not expected to be mobile in soil. Under conditions of continual release high silver levels may accumulate in soil because of the metal's immobility and inability to be degraded.

The primary known cultural source of silver to POTWs is the photographic industry. Typical levels in effluents are below concentrations thought to inhibit activated sludge processes. Amateur photographers may discharge significant quantities of silver to POTWs in discarded solutions. The impact of these releases is reduced by dilution in sewers before reaching the POTW. On a national scale, these releases do not constitute a very large amount of silver discharge.

Silver is acutely toxic to aquatic organisms at concentrations as low as 0.5 ug/l, while chronic and sublethal effects have been observed upon exposure to 0.2 ug/l.

The lowest LC_{50} reported for freshwater vertebrates, is 4.3 ug/l (for guppies), while acute effects in freshwater invertebrates have been recorded at concentrations as low as 1.5 ug/l for Daphnia magna (LC_{50}). The threshold level for chronic damage to rainbow trout (Salmo gairdneri) is 0.2-0.8 ug/l, while the chronic LC_{50} value for the embryos of this species is 10 ug/l. Similar concentrations of silver produce chronic effects in freshwater invertebrates.

No data were available on the acute or chronic effects of silver on marine vertebrates. Among marine invertebrates, concentration of 0.5 ug/l produced acute effects in the sea urchin and 2 ug/l produced chronic effects in an echinoderm.

Water hardness is an important variable influencing the concentrations of silver producing acute and chronic effects in aquatic biota. In fact, the EPA Ambient Water Quality Criterion for protection of freshwater aquatic life from silver is expressed as a function of water hardness at a particular location. At hardness of 50, 100 and 200 mg/l as $CaCO_3$ the concentration of silver (total) should not exceed 1.2, 4.1 and 13 ug/l, respectively, at any time. Figure 15 and Appendix B include maps of locations in the U.S. where violations of the hardness-related water quality criterion for protection of aquatic life were found.

Data on the effects of silver on terrestrial animals were limited. Chronic exposure studies for birds and mammals indicate effects that include ventricular hypertrophy, skin discoloration, lowered immunological activity, and altered membrane permeability.

Silver concentrations of 4900 ug/l have been fatal to terrestrial plants (lupines). Soil organic matter affects the phytotoxicity of silver.

Microorganisms (bacteria, yeast, and fungi) have been killed in 2-24 hours by silver concentrations as low as 1 ug/l. Silver may be added to water at levels of 0.5 ug/l or higher to act as a general bactericide. The form of silver is an important variable in toxicity. A mixed population of microorganisms in soil showed a significant reduction in activity at 60 ug/g of AgI but not at an equivalent concentration of $AgNO_3$. In sludge populations, microbial activity was reduced following exposure to silver at levels ranging from 1.0 ug/g up to 500 ug/g, depending on the compound.

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CHAPTER VI.

EXPOSURE AND EFFECTS--HUMANS

A. HUMAN EXPOSURE

1. Introduction

The most commonly reported effect of human exposure to silver is the occurrence of argyria, a bluish-gray pigmentation of the skin. Cases have been documented that associate the condition with dermal contact, ingestion, and inhalation. Thus, all three major routes by which humans can be exposed to silver can be important. This section considers human exposures via ingestion, dermal contact, and inhalation.

The major sources of ingested silver are foods and accidental ingestion of silver-bearing products (e.g., silver beads, bearings, and jewelry by children). Since concentrations of silver in surface, well, and tap waters are typically below detection limits, drinking water does not represent a major exposure route for humans. Dermal absorption of silver occurs as a result of medicinal applications, occupational exposure, handling of jewelry and other silver objects (e.g., silver flatware, trophies, bowls, etc.), and contact with photographic developing and fixing solutions. Inhalation of silver is an exposure route in urban areas, and in the vicinity of silver mines, steel mills, and ore smelters.

2. Ingestion

a. Food

Silver exists as a normal trace constituent in many foods in varying concentrations presented in Table 48. Silver has been detected in food items in concentrations ranging from 2.0 ug/g in crustaceans to 0.007 ug/g in legume and root vegetables (Table 48). When these concentrations are combined with average daily consumption levels for each food group (U.S. FDA 1974), the average daily intakes shown in Table 48 can be calculated for each group. As can be seen in Table 48, individuals who consume large amounts of mushrooms, mollusks, crustaceans, and bran will ingest more silver than those who consume less silver-intensive foods.

The Water Quality Criterion Document (U.S. EPA, 1979) indicates that daily dietary intake of silver in the United States ranges from 35 ug/day to 88 ug/day (see Table 49). There is a small difference in intake levels for men and women. These estimates are calculated based on typical rather than maximum silver concentrations in food and assume average dietary patterns and thus are expected to better represent the general U.S. population

TABLE 48. ESTIMATED SILVER INGESTION IN FOODS

Food Group	Average Consumption (g/day)	Average Concentration Silver (ug/g)	Average Silver Intake (ug/day)
Dairy	763[1]	0.027-0.054[2]	20.60-41.20*
Meat, Fish and Poultry, Total	267[1]	0.004-2.00[3 4 5]	1.07-534.00
Beef		0.004-0.024[3]	**
Beef Liver		0.005-0.194[4]	**
Pork		0.007-0.012[3]	**
Mutton & Lamb		0.006-0.011[3]	**
Crustaceans		2.0[5]	**
Trout		0.48-0.99[6 7]	**
Mollusks		0.1-10.0[5]	**
Grains, Cereals, Brans	422[1]	0.4-1.00[8]	168.80-422.00
Potatoes	183[1]	0.005-0.012[9]	0.92-2.20
Leafy Vegetables	55[1]	N.D.-0.008[9]	0-0.44
Legume Vegetables	69[1]	0.0029-0.0073[9]	0.20-0.50
Root Vegetables	33[1]	0.0062-0.0075[9]	0.20-0.25
Garden Fruits	92[1]	N.D.[9]	-
Fruits	221[1]	N.D.[9]	-
Mushrooms	55[1]	5.5[10] "Several hundred ppm"[11]	300-5,500
Oils &Fats	72[1]	N.I.	-
Sugars	82[1]	0.001-0.030[12]	0.08-2.46
Beverages	712[1]		
Water		0.03[13]	60:00
Coffee		0.02[14]	
Tea		0.20-2.00[14]	
Total - Based on Dietary Analysis of Husband and Wife		Range 18-103[15] Mean: 35 male, 44 female[15]	

1. U.S. FDA (1974)
2. Murthey and Rhea (1966)
3. Armour Research Foundation (1952)
4. Masironi (1974)
5. Boyle (1968)
6. Tong *et al*. (1974)
7. Freeman (1977)
8. Kent-Jones and Amos (1957)
9. Oakes *et al* (1977)
10. Allen and Steinnes (1978)
11. Ramage (1930)
12. Hamilton and Minski (1973)
13. U.S. DHEW (1970)
14. Vanselow (1966)
15. Tipton *et al*. (1966)

*Only available data concern the concentration of silver in milk. Because milk is a constituent of cheese, butter, etc., this was used for an extreme case determination of total silver consumption. However, this neglects eggs and other "dairy" products that may have varying silver concentrations.

**Since Food Group consumption was presented for the group as a whole and not by food type, associated silver consumption for the meats are combined into one number on meat, fish and poultry.

than a compilation of estimates from Table 48. Therefore, the total diet levels are used to estimate human risk in Chapter VII.

TABLE 49. ESTIMATES OF DAILY SILVER INTAKE IN HUMAN DIET

Amount of Silver Ingested Daily (ug/day)	Population	Reference
0.4	3 Italian populations	Clemente et al. (1977)
27	Population in U.K.	Hamilton and Minski (1973)
35	Man (U.S.)	Tipton et al. (1966)
44	Woman (U.S.)	Tipton et al. (1966)
70	Reference man (U.S.) (average intake)	Snyder et al. (1975)
88	Not given	Kehoe et al. (1940)
30	Reasonable estimate based on preceeding results	U.S. EPA (1979)

Source: U.S. EPA (1979).

Tipton et al. (1966) conducted a 30-day diet study on two human subjects, monitoring trace element concentrations in food and excreta, ingestion rates of food and liquids, and excretion rates. Estimated daily intake rates for silver (30-day average) were 35 ug and 44 ug of silver for the male and female subjects, respectively. The average daily excretion rate (in urine and feces) was 89 ug and 37 ug, respectively. This resulted in a balance (+7 ug) for the female but a significant negative balance (-54 ug) for the male subject. The results indicate an efficient removal mechanism for ingested silver from the body. In the case of the male subject the negative balance evidently resulted from uptake of silver from other unaccounted sources (e.g., inhalation of air, amateur photography) or metabolism of silver deposits already contained in the body. The intake rates from food and water were on the same order of magnitude as the other ingestion estimations reported in Table 48.

Sludge-amended soil used to grow agricultural produce contains silver in concentrations as much as 10 times greater than normal soils (U.S. EPA 1979). Sewage sludge has been reported to contain as much as

900 mg/kg although typical concentrations are much lower, around 100 mg/kg (Smith and Carson 1977). Plants have been observed to take up silver from solution under experimental conditions (see Chapter IV-D). Also uptake has been reported to be related to soil concentration (Smith and Carson 1977). However, no laboratory studies were available on uptake from sludge-amended soil nor reports of concentrations in crops grown on sludge-amended fields. Therefore, it is not possible to ascertain how significant this exposure route is to humans.

Weather modification techniques utilize silver iodide as a nucleating agent. Precipitation associated with this process deposits some portion of the seeded silver iodide on plants and soils, which may then enter the food chain (Jones and Bailey 1974). However, monitoring studies show that media silver concentrations resulting from cloud seeding are not significantly greater than normal background levels with extreme levels 200 times as great (Teller et al. 1974). Therefore, this activity is not expected to contribute to increased human exposure in areas subject to weather modification. Additionally, the use of silver in weather modification activities has declined recently.

b. Water

The U.S. Public Health Service Standard and EPA Water Quality Criterion for human health are 0.05 mg/l (U.S. EPA 1980b). The Food and Drug Administration also has a 0.05 mg/l criterion for bottled waters (U.S. EPA 1979). A consumption of 2 liters per day of water containing this level of silver would result in a daily intake of 0.10 mg.

Silver has been used as a bactericide to purify potable waters carried by tankers, drilling rigs, and airlines. Some water bottlers also use it for this purpose. In 1978, 19 companies were registered by the U.S. EPA to manufacture filters containing silver to purify waters; this represented almost a doubling from the number registered in 1976 and suggests that the use of silver for this purpose may be increasing (U.S. EPA 1979).

Water supplies (surface waters, wells, and tap waters) that have been monitored for existence of trace elements consistently contain silver at concentrations below the EPA Water Quality Criterion for human health of 0.05 mg/l. The silver concentrations found in various waters are presented in Table 50 and discussed in Chapter IV-E.

The U.S. Department of Health, Education and Welfare (1970) reported that the maximum concentration of silver found in community water supplies was 0.03 mg/l (in 2595 samples taken at the tap). The maximum human ingestion based on consumption of 2 l water containing this concentration would be 0.06 mg of silver per day. In STORET, the maximum silver concentrations reported for major river basins ranged from 0.095 mg/l to 0.790 mg/l (STORET 1980). The ingestion of these waters without further treatment would provide an individual with 0.188-1.580 mg/day of silver.

TABLE 50. CONCENTRATIONS OF SILVER DETECTED IN DRINKING WATERS

Sample	Concentration (mg/l)		Reference
	Range	Mean	
Tap Water	-	0.0260	Smith and Carson (1977)
Tap Water	-	0.0300 (max.)	U.S. DHEW (1970)
Bottled Water	-	0.0500 (FDA recommended)	44 FR 12169 - U.S. FDA (1979)
Water-(Gen. U.S. monitored-maximums)	0.0940-0.790	-	STORET (1980)
Well Water	0.0001-0.0004	0.0002	Bradford (1971)
Well Waters (Gen. U.S. monitored)	0-0.0300	0.0140	STORET (1980)

For well waters, the 2,232 observations in STORET over a two-year period indicated a mean concentration of 0.014 mg/l and a maximum of 0.030 mg/l. The exposure associated with ingestion of these waters would be 0.028 mg/day and 0.060 mg/day, respectively.

c. Products Containing Silver

There is a potential, especially for small children, to ingest silver objects. However, due to the probable inert form of silver in the ingested object (ball bearings, small jewelry) and the inefficiency of uptake from the gastrointestinal tract, this route of exposure is not expected to be significant.

3. Dermal Contact

a. Medicinal Applications

Through the end of the 19th century, silver nitrate was widely used medicinally. With the increased development of more advanced drugs in the 20th century, the application of silver nitrate for medicinal purposes decreased. More recently, the medical community has begun to reevaluate silver nitrate for local applications such as the treatment of burns (U.S. EPA 1979).

Argyrol solution, which consists of a colloidal preparation of silver oxide in a casein, alkaline gelatin or serum albumin solution, was invented in 1902, but Crannel (1975) reports that it is still widely used as a local disinfectant. Argyrol solution contains 19-23% silver and recommended applications are 5-50% Argyrol concentration. The maximum amount of silver in a 1-ml application of Argyrol would be 100 mg. Other silver-containing solutions include Protargol and Neo-Silvol; their prescribed application would result in about the same dermal exposure used to the same amounts as the compounds described previously (Crannel 1975).

Silver is a constituent of dental amalgan along with tin, copper, and zinc. Although amalgam is as much as 67 to 70% silver, it is mixed with mercury for application, reducing the silver concentration in dental fillings to 33% (Crannell 1975). Lierskar (1974) found in vitro release of some silver from amalgam dental fillings into a human monolayer epithelial cell culture (up to 0.02 ug Ag/ml at 3 days). Hals (1976), however, reports that in real situations because of the nature of teeth restorations and the composition of amalgam, little silver is released to the surrounding tissues in the mouth. One case study documented effects of absorption of dental silver resulting in localized argyria. A crown with one-third silver alloy filling was placed on a primary tooth. The site of the tooth exhibited grey stained tissue. Pigmentation was attributed to the impregnation of adjacent tissues with silver particles (Burton 1972). Due to the small total amount of silver available for uptake and the low translocation rate of silver in mammals following silver uptake (U.S. EPA 1979), this exposure route is not expected to be significant in terms of more than local effects.

b. Photography

One of the more prominent human exposures to silver, in terms of total silver mass involved, is through film development and printing; however, in terms of the amount actually absorbed into the body, the exposure does not appear to be very significant.

A home developer works with developing and fixing solutions which may accumulate 16g of silver or more in the course of a single developing session. This assumes 1.5g silver per m of film, 2 m per roll, and that six rolls are developed in one session. Exposure to silver could occur through dermal contact or, more remotely, through inhalation.

Two factors suggest that dermal absorption is not a significant exposure route beyond potential development of localized argyria. First, most home developers wear gloves or use implements to avoid direct contact with the solution. Second, observation of individuals with argyria indicate that the primary concentration of silver remains in the surface layer of the skin (Buckley 1963). A woman exposed to fixing solution (no concentration given) over a period of several months developed discoloration on the skin actually in contact with the solution; no other effects were reported. The author noted that occurrences such as this one were unusual due to low silver concentrations in fixing solution and the common practice of wearing gloves when using fixer.

Due to the low volatility of silver, inhalation is not expected to expose amateur photographers to significant levels of silver. No specific information on this subject was available.

c. Industry

Few reports of industrial releases and associated occupational exposures to silver are found in the literature. One case related to the silver mining industry concerns of an individual who worked in the mines for 20 years during the last part of the 19th century. Within 5 years after he had stopped working there, his entire body was a "deep blue, and from a distance appeared almost black." He was diagnosed as having generalized argyria as a result of dust accumulation on the skin and/or inhalation (U.S. EPA 1979). Further discussion of industrial exposure can be found in Carson and Smith (1977) and NAS (1977).

d. Jewelry and Sterling Silver

Silver jewelry such as rings, bracelets, necklaces, and earrings obviously are in frequent contact with the skin. No work has been done to estimate quantities of silver released as a result of skin contact nor have there been any indications of adverse health or cosmetic effects. The uptake rate of silver by intact skin has been reported as low (U.S. EPA 1979).

e. Swimming Pools

Silver chloride (at concentrations as high as 150 ug/l) has been used as a bactericide in swimming pool applications. Also some U.S. swimming pools use activated carbon filters coated with metallic silver, effecting water concentrations of 20-40 ug/l (U.S. EPA 1979). However, these uses are believed to have decreased significantly due to cost (NAS 1977). Two factors contribute to this circumstance: regulations have restricted the use of silver compounds in potential skin-contact applications to prevent outbreak of argyria; and advances in chlorination techniques have decreased the use of silver. Also there is very little evidence for uptake of silver by intact skin (U.S. EPA 1979). Therefore, the exposure of humans to silver in swimming pools is assumed to be negligible.

4. Inhalation

Silver is inhaled by many individuals at ambient concentrations and by much small subpopulations in special situations at higher levels. Ambient atmospheric concentrations are presented in Table 51 with rates of daily inhalation. The available data indicates that the most significant atmospheric exposure is in locations adjacent to or in close proximity to smelters (Ragaini 1977) and steel mills (Harrison et al. 1971). The typical respective intakes of silver in these locations would be 453.6 ng/day and 21.6-216.0 ng/day, respectively, and might be as high as 1576.8 ng/day near smelters. High air concentrations of silver were found near the San Francisco Mint, in which daily exposure is 0.86 mg/day (note shift in units). Presumably, this is an occupational exposure and would not be continual over a 24-hour period; therefore, the intake by inhalation would be 0.29 mg/day (U.S. EPA 1979).

The urban atmosphere will provide its residents with fairly consistent amounts of silver ranging from 47.5 ng/day in non-industrial Washington D.C. to 185.8 ng/day in heavily industrial Chicago. San Francisco had relatively lower exposures to silver, only 2.2-8.6 ng/day Non-urban and rural locations generally have lower atmospheric loads of silver.

The literature indicates that dust particles from mines producing silver and ores in which silver is a byproduct could provide a potential occupational exposure, as can metal working shops. No data were available to quantify exposure by this route.

Soldering, especially at high temperatures, releases silver to the atmosphere during the stage in which the solder is heated and applied. The magnitude of this release depends upon the scale of the operation and the concentration of silver in the solder. Inhalation exposure of both industrial workers and jewelry soldering hobbyists may result from this activity. Large-scale industrial soldering shops would provide a larger and more consistent release than domestic use. Daily intake of silver through inhalation in the workplace is restricted by

TABLE 51. ESTIMATED SILVER INTAKE BY INHALATION

Source	Atmospheric Silver Concentration (ng/day)		Silver Inhaled (ng/day)		Reference
	Range	Mean	Range	Mean	
Urban Areas					
Washington, D.C.	-	1.1	-	47.52	Trout (1975)
Chicago, IL	-	4.3	-	185.76	Brar *et al.* (1970)
San Francisco, CA	0.05-0.2	-	2.16-8.64	-	John *et al.* (1973)
Glasgow, UK	0.3-12.9	2.7	1.30-557.28	116.64	McDonald and Duncan (1979)
Heidelberg, Germany	-	4.2		181.44	Bogen (1974)
Steel Mills - East Chicago	0.5-5.0	-	21.60-216.0	-	Harrison *et al.* (1971)
Smelter - Kellog, Idaho	0.94-36.50	10.5	40.61-1576.80	453.60	Ragaini *et al.* (1977)
San Francisco Mint		0.02 mg/m^3	-	9.86 mg	Anania and Seta 1973
Other Areas					
Nebraska	-	0.15	-	6.48	Struempler (1975)
Chicago, IL	1.0-2.4	-	43.2-103.68	-	Bogen (1974)
Oak Ridge, TN		0.17	-	7.34	Andren *et al.* (1974)

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[1] Assuming an inhalation rate of 1.8 m^3/hr and 24 hours per day.

OSHA to 100 ug/day (0.01 mg/m^3 x 10 m^3 per workday) (U.S. EPA 1979). The significance of domestic exposure of hobbyists could not be determined, but due to the small amounts of silver used in soldering, the resulting silver concentration in air is expected to be very small and less than the OSHA limit.

B. HUMAN TOXICITY

1. Introduction

The ingestion of silver, even in trace quantities, has no known beneficial effects as an essential micro-nutrient (NAS 1977). Silver, however, has been used since antiquity for various medicinal purposes. Various silver compounds have been utilized as preservatives, astringents, nose drops, mouthwashes and as remedies for gastrointestinal disorders. Instillation of 1% silver nitrate solution into the eyes of newborn infants is still legally required in many states for prophylaxis of gonorrhea and silver nitrate and silver sulfadiazine are used in the topical treatment of severe burns as protection against infections with gram-negative bacteria (Grier 1977). Because of its bactericidal activity, the silver ion has also been added to drinking water for disinfection purposes (NAS 1977).

2. Metabolism and Bioaccumulation

a. Absorption

The metabolism of silver in man and animals has not been extensively studied due to poor absorption by all routes of administration. A maximum of 10% of ingested silver salts is absorbed in mice, rats, monkeys and dogs (Furchner *et al*. 1968); there are no precise data available for man. Poor gastrointestinal absorption is attributed to the sparingly soluble nature of most silver salts; the soluble sulfate and nitrate salts are converted to insoluble chlorides in the stomach (Venugopal and Luckey 1978). Absorption via inhalation is also believed to be low, although there are no quantitative data concerning the extent of absorption via inhalation (Fowler and Nordberg 1979).

Some absorption has been demonstrated via mucous membranes or non-intact skin, but absorption through intact skin is poor, presumably due to the binding of the silver ion to skin proteins (Petering 1976). Wahlberg (1965) reported less than 1% absorption of a silver nitrate solution (25.8 mg Ag/ml) applied to intact skin of guinea pigs. Several similar studies indicating poor absorption through intact skin were reviewed by Hill and Pillsbury (1939). With respect to broken skin, Harrison (1979) reported that peak attachments of Ag^{110}- labeled sulfadiazine silver to the burn wounds of humans and rates were 1% and 8% of the dose, respectively, within 24 hours. Dissection of the wounds showed 81-98.7% of the attached silver was present in the most superficial layers of cells. Similarly, Constable and co-workers (1967) found that the majority of 0.5% silver nitrate solution applied to open wounds (3.5 x 3.5 cm^2) on the backs of guinea pigs for 5 days remained in the general area of the wound but with some absorption evident in liver and kidney. Daily skin application of a saturated solution of colloidal silver and silver oxide to the depilitated backs of rats for 3 months resulted in findings of 1.54 mg/kg silver in kidney, 1.50 mg/kg in spleen, 0.16 mg/kg in liver plus traces in heart and lungs (Desquidt et al. 1974). Additional data on the dermal absorption of silver, particularly with respect to burn therapy, can be found in the U.S. EPA Criterion Document for Silver (1979).

Parenterally injected silver salts remain at the site of injection bound to tissue proteins; only a fraction of the dose is actually absorbed (Venugopal and Luckey 1978). Large doses of intravenously administered silver compounds produce hemolysis and agglutination of erythrocytes; at lower doses, silver complexes with serum albumin and is transported to the tissues (Venugopal and Luckey 1978).

b. Excretion

In mammals, excretion of silver is almost entirely fecal (reflecting poor absorption), with a trace in urine. For example, 70% of an intravenous dose (0.1 mg ^{110}Ag/kg) of silver was eliminated in rat feces within 4 days (45 % in the first 24 hours) with less than 0.5% of the dose found in urine during this time period (Klaassen 1979). Of the abosrbed silver, over 90% is excreted via the feces in mice, rats, monkeys, and dogs given radioactive ^{110}Ag (as the nitrate by the oral, intravenous or intraperitoneal routes (Furchner et al. 1968). The fecal elimination of absorbed silver is mainly explained by biliary excretion.

Furchner et al. (1968) reported an increased renal excretion and a concomitant reduction in fecal excretion of silver in laboratory animals following bile duct ligation. Klaassen (1979) measured the disappearance from plasma and excretion into bile of ^{110}Ag following intravenous injection of rats with 0.01, 0.03, 0.1 or 0.3 mg ^{110}Ag/kg. Biliary concentrations peaked within 30 minutes of administration, then slowly decreased with time. Over a 2-hour interval, 25-45% of the administered silver was excreted into the bile. The ratio of bile to plasma ^{110}Ag concentrations was 16-20 to one.

A similar comparison between the disappearance of silver from plasma and its excretion into bile following intravenous injection of 0.1 mg ^{110}Ag/kg into rats, rabbits, and dogs revealed marked species variation in the biliary excretion of silver. The rat excreted silver into bile at a rate about 10 times that of the rabbit and about 100 times that of dogs. This difference is due to the concentration of silver in bile rather than the rate of bile production and appears to be associated with species differences in the rate of transfer of silver from liver to bile; i.e., at 2 hours, silver concentrations in liver were 1.24, 2.13 and 2.90 ug Ag/g tissue for the rat, rabbit and dog, respectively (Klaassen 1979).

The biological half-time for silver in the lungs was on the order of 1 day for a man who accidently inhaled ^{110m}Ag dust; the half-time for the liver was 52 days (Newton and Holmes 1966). No silver was detected in urine during the first 50 days, but it was present in fecal samples up to about day 300. Similarly, an apparent biological half-life of approximately 1 day was found by whole-body scintillation counting in mice, rats, dogs and monkeys after oral administration of ^{110}Ag, which is partially attributable to fecal elimination of unabsorbed silver (Furchner et al. 1968). Somewhat longer half-lives were observed after intravenous administration in monkeys (1.8 days) and dogs (2.4 days) (Habighorst and Buchwald 1971).

c. Tissue Accumulation

Based on the data of Tipton and Cook (1963), the average silver content in tissue of normal Americans is about 0.005 ug/g wet weight. The highest concentrations of silver are usually found in the liver, spleen and to some extent in brain, muscle and skin (NAS 1977). Hamilton et al. (1973) reported concentrations of 0.008, 0.006, 0.004, 0.002 and 0.002 ug/g wet weight for blood, liver, brain, kidney and lung tissue, respectively. Indrapraist et al. (1974) found 0.4, 0.7 and 2.7 ug/g on a dry weight basis in kidneys, liver and spleen of normal people. Creason et al. (1976) reported silver concentrations of 0.5 ug/100g in placental tissue and 0.4 and 0.5 ug/100 ml in maternal and cord blood, respectively.

Newton and Holmes (1966) reported more than 50% of the body burden of silver was found in the liver of an individual 16 days after accidental exposure to radioactive silver.

Silver apparently accumulates in the body with age (Venugopal and Luckey 1978, Smith and Carson 1977) but the nature, site and extent of accumulation are not definitely known. Based on an average human dietary intake of 88 ug/day (Kehoe et al. 1940), and assuming 100% absorption of ingested silver, Smith and Carson (1977) estimated that it would require 31 years to accumulate 1g of silver. However, if the average tissue content of silver in normal Americans is .005 ug/g wet weight (Tipton and Cook 1963), then the tissue content of the average individual (68 Kg) at this concentration would only be 32 mg of silver or 3.2% of a 31-year ingestion total (Smith and Carson 1977).

3. Human and Animal Studies

a. Carcinogenesis

Oppenheimer and co-workers (1956) subcutaneously injected two 1.5-cm silver foil circles or squares into the abdominal wall of 25 male rats; there were no control animals. Fourteen of the treated rats (32%) developed fibrosarcomas at the injection site between 275 and 625 days. Similarly, subcutaneous implantation of 17-cm diameter silver disks into rats (8 disks/rat) resulted in sarcomas in 65 of 84 rats by 23 months (Nothdurft 1956). No sarcomas were seen, however, in a lifetime study in which 35 rats were subcutaneously implanted with silver foil fragments (1x1x0.02 mm). There were 24 survivors at 18 months (Nothdurft 1958).

Schmaahl and Steinhoff (1960) found 8 of 26 (31%) surviving rats injected subcutaneously or intravenously with divided doses of a colloidal silver suspension over an 8-month period (total dose 65 mg Ag/rat) developed malignant tumors. Tumors included six sarcomas at the injection site, one leukemia and one laminar epithelial carcinoma; the average latency period was 695 days. The physical state of the compound probably played a role in the development of tumors.

In contrast, Furst and Schlauder (1977) found no tumors in rats at 2 years following repeated monthly intramuscular injections with 300-mesh silver powder suspended in trioactanoin. The total dose was 75 mg Ag/rat.

In a skin tumor promotion study with the carcinogen 7, 12-dimethylbenz(a)anthracene (DMBA) (1.5%) mice were treated dermally with aqueous silver nitrate twice a week for 44 weeks following initial treatment with DMBA. Three of 13 survivors at 20 weeks developed eight pipillomas (but no carcinomas) with an average latent period of 19 weeks. Silver nitrate was judged to cause marked epidermal hyperplasia (Saffiotti and Shubik 1963).

Thus, there are no indications that exposure to silver by the normal intake routes is carcinogenic. Although several studies have demonstrated tumor induction by implantation of silver foils or disks, carcinogenesis resulting from injections or implantation in which the tumors are induced only at the site of application are generally regarded as irrelevant to human exposure.

b. Mutagenesis

Several bacterial mutagenicity assays with various silver salts have proved negative. Demerec et al. (1951) reported negative findings in Escherichia coli with 0.000005 to 0.0001% silver nitrate solution. Similarly, Clark (1953) reported negative effects in Micrococcus pyogenes var. *aureus* exposed to 0.000001% $AgNO_3$. In a rec-assay[1] with *Bacillus subtilis*, Nishioka (1975) also noted negative results with 0.72% AgCl solution.

Sirover and Loeb (1976), however, reported that 0.0005% $AgNO_3$ altered fidelity of DNA synthesis *in vitro* (i.e., increased the error frequency by greater than 30%). They, therefore, designated silver as a suspect carcinogen.

Recently, Casto *et al.* (1979) also reported that $AgNO_3$ enhanced transformation of Syrian hamster embryo cells by a simian adenovirus, SA7. An enhancement ratio of 2.7 above control was recorded for a 0.001% concentration of $AgNO_3$ after 18 hours exposure.

Thus, the data concerning mutagenicity are conflicting. Bacterial assays with relatively low concentrations of silver salts are negative, while a test with mammalian cells at somewhat higher concentration indicated some enhancement of cell transformation. Additional work is needed to clarify this issue.

c. Adverse Reproductive Effects

Little is known concerning the effects of silver on reproduction and/or embryonic development. Barrie (1976) reported the absence of the left fibula and right ulna and related limb-reduction defects in an infant born to a mother who conceived and maintained a pregnancy with a Grafenberg ring intrauterine device *in situ*. The intrauterine device was stated to be composed mainly of German silver. Thrush *et al.* (1968), however, report that German silver is composed of nickel, copper, and zinc but no silver.

Freeman and Coffey (1973) injected 10% silver nitrate solution directly into the vas deferns of eight mature Sprague-Dawley rats. Subsequent mating with female rats beginning 2 weeks after treatment for a period of 8 months indicated complete sterility in males. Histological studies of the vas deferens showed the lumen completely replaced by scar tissue and the complete absence of sperm. Similar treatment of a dog produced the same pathologic lesions. The pathology associated with direct injections of a caustic solution of silver nitrate into the testes of rats and dogs, however, has little significance to human risk from ingestion of silver salts.

d. Other Toxic Effects

The toxicity of the silver ion is attributed to its ability to form stable complexes with structural and functional proteins, and thereby disrupt life processes. The data available on the toxic effects of silver to humans are meager. The limited systemic effects of silver are due, at least in part, to the poor absorption of silver from the intestinal tract (Furchner *et al.* 1968), through intact skin (Petering 1976), and presumably, via inhalation (Fowler and Nordberg 1979).

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[1] A method for screening chemical mutagens which observes differential growth sensitivities to chemicals in wild and recombination-deficient strains of bacteria.

i. Animal Studies

Intravenous injections of colloidal silver or silver salts have routinely been used to induce acute pulmonary edema in dogs for study purposes (NAS 1977, U.S. EPA 1979). Intravenous injections of laboratory animals with silver compounds are principally associated with effects on the central nervous system: weakness, rigidity, contractures of the legs, loss of voluntary movements and interference with cardiac hemodynamics (Hill and Pillsbury 1939). Fifty percent lethal dose (LD_{50}) values of 100 mg/kg and 420 mg/kg, respectively, have been recorded for colloidal silver following oral exposure in the mouse (Venugopal and Luckey 1978) and intraperitoneal injection in the rat (Desquidt et al. 1974). Pretreatment of ICR Swiss mice with the silver ion (4/10 LD_{50}ip) 48 hours prior to an LD_{50} study afforded protection by significantly increasing the LD_{50} value by intraperitoneal injection to 18 (16.6-19.4) mg Ag/kg in contrast to a value of 12.5 (10.4-15.1) mg Ag/kg for mice without prior exposure. Pretreatment is believed to induce the synthesis of metallothionein, a metal-binding protein (Jones et al. 1979). Additional studies on the acute effects resulting from injection of silver salts into laboratory animals can be found in Smith and Carson (1977) and U.S. EPA (1979).

The primary toxic effects of chronic silver exposure in animals are seen in the cardiovascular, hepatic and, hematopoietic systems (Fowler and Nordberg 1979). Olcott (1950) reported hypertrophy of the right ventricle and thickening of the glomerular membrane, presumably due to vascular hypertension, in rats given 635 mg Ag/L (as $AgNO_3$) or 660 mg Ag/L (as $Ag_2 S_2O_3$) in their drinking water for up to 30 months.

Deposits of silver granules in the glomeruli and tubules of the kidney, as well as pathological changes in renal tubules, were reported by Fuchs and Franz (1971) in rats given 0.2% silver nitrate in their drinking water from 10 to 50 weeks. Similar findings were reported by Day et al. (1976) and Brozman et al. (1976) in rats administered 0.1% or 0.2% silver nitrate, respectively, in drinking water for 3 months.

Albino rats given 0.05 mg Ag/l in drinking water showed no changes in gastric secretions, blood serum enzymes, or liver and kidney morphology at 5 months nor in conditioned-reflex activity at 11 months (Barkov and El'piner 1968). Savluk and Moroz (1973) noted no changes in hematogical parameters or liver function in rats ingesting 0.2 mg Ag/l in drinking water for 3 months and exposure to this concentration for 6 months reportedly produced no effect on conditioned-reflex activity in rats (Kharchenko and Stepaneko 1972).

Additon of 0.4 mg Ag/l to the drinking water of rats for an indeterminant time period was stated to have produced small hemorrhages in rat kidneys (Just and Szniolis 1936). At a drinking water concentration of 0.5 mg Ag/l, lowered nucleic acid content was seen in rat brain tissue at 6 months (Kharchenko et el. 1973), reduced conditioned-reflex activity in rats at 11 months (Barkov and El'piner 1968), lowered immunological resistance in rabbits at 11 months (Barkov and El'piner 1968) and increased brain weight in rats at 12 months (Kharchenko et al. 1973). Pathologic changes in vascular, nerve, brain, and spinal cord tissues were also observed in animals at the 11-month mark (Barkov and El'piner 1968). Additional details on a variety of studies, conducted predominantly in the USSR, in which silver ion was added to the drinking water of laboratory animals can be found in U.S. EPA (1979). In essence, adverse effects associated with the ingestion of silver in drinking water are generally evident in laboratory animals at concentrations greater than 0.2 mg Ag/l.

ii. Observations in Man

Acute toxic effects from silver in humans generally occur only from accidental or suicidal overdoses (Smith and Carson 1977). Ingestion of 10 g of silver nitrate is usually fatal in humans but 30 g have been survived (Hill and Pillsbury 1939). Acute toxic symptoms following ingestion of caustic silver nitrate include severe gastroenteritis, diarrhea, fall in blood pressure, decreased respiration, spasms, paralysis and eventual death depending on the level of exposure (Venugopal and Luckey 1978).

Hill and Pillsbury (1939) reported lethal responses to therapeutic intravenous injections of 50 mg or more of Collargol (~0.7 mg Ag/kg). Pulmonary edema, hemorrhage and necrosis of bone marrow, liver and kidney were observed upon post-mortem examination. Intrauterine administration of approximately 25 g of silver nitrate also was reported to be rapidly fatal (Reinhart et al. 1971).

Dressings soaked with 0.5% $AgNO_3$ have been extensively used in the treatment of burns without any evident local or systemic silver toxicity (Hartford and Ziffren 1972). Electrolyte imbalances (due to a tendency of precipitate AgCl) have been reported in burn patients treated with silver sulfadiazine (Burke 1973). Leukopenia was also once indirectly associated with treatment of burn patients with silver sulfadiazine but is now known to result from thermal injury and not the treatment (Kiker et al.1977).

There is also a report in the literature of an allergic reaction to silver amalgams, which manifested itself as peridontal disease in a 52-year-old woman (Catsakis and Sulica 1978).

Prolonged intake of low doses of soluble silver salts can produce a variety of toxic effects in man including fatty degeneration of liver and kidney, changes in blood cells, irritation of the skin, eyes and intestinal tract and both localized and generalized argyria (NAS 1977). Argyria is an unsightly, permanent blue-gray pigmentation of the skin, hair, fingernails, mucous membranes, and eyes resulting from the deposition of microscopically detectable silver-containing granules in the dermis, hair follicles and/or sebaceous and sweat glands and is most pronounced in areas exposed to light (Venugopal and Luckey 1978). Deposition also occurs in the cornea (often seen as a blue halo) and anterior capsule of the lens but not in the optic nerve (Fowler and Nordberg 1979). In localized argyria, only limited areas are pigmented. Although generally considered a cosmetic defect with no significant physiologic effect, some investigators maintain that deposition of silver in the kidney is associated with arteriosclerotic changes and deposition in the eye, with impairment of vision, particularly night vision (NAS 1977). Zech et al. (1973) attributed a nephrotic syndrome with associated proteinuria in a 73-year-old argyric man to the use of a silver-containing mouthwash for 10 years. There is no recognized effective treatment for argyria; chelation therapy is ineffective (Lehnert 1973).

In an examination of 30 employees of an industrial plant involved in the manufacture of silver nitrate and silver oxide, Rosenman et al. (1979) noted that the majority of workers complained of eye and both upper (nose and throat) and lower (cough, wheezing and chest tightness) respiratory tract irritation, usually on a daily basis. Other complaints included nausea (23% of the workers), headaches (30%), nervousness (33%), tiredness (30%) and abdominal pain (33%). Abdominal pain was found to be significantly associated with detectable levels of Ag in blood: median 1.95 ug/100 ml, range 1.1-84. ug/100 ml.

In a follow-up of these workers, Moss et al. (1979) examined them for the frequency and extent of ocular argyria. Pigmentation of the conjunctiva was present in 20 workers and corneal pigmentation in 15. A direct relationship was found between the level of pigmentation and duration of employment. Ten workers noted decreased night vision but no structural deficits could be found in seven workers.

Although never common, generalized argyria is rarely seen today due to improved work conditions. The exposure conditions giving rise to argyria have not been well defined. Estimates from industrial exposures indicate gradual accumulation of between 1g and 8g Ag by inhalation (Hill and Pillsbury 1939) or ingestion of 1 to 30g soluble silver salts (Lehnert 1973) will lead to generalized argyria. Instillation of 0.25% $AgNO_3$ into the eyes for 3 weeks has been reported to result in localized argyria (Hill and Pillsbury 1979). The National Academy of Sciences (1977) calculated that consumption of 2 l of drinking water containing 50 ug Ag/l, a concentration several fold higher than that normally found in U.S. drinking water, and an assumption of 50% retention of intake, would result in the retention of 50 ug Ag per day or 1g Ag in 55 years (borderline argyria).

e. Interactions With Selenium, Vitamin E, Copper

Coverage of all the potential interactions of silver with other compounds are beyond the scope of this report. However, the accentuation or mitigation of a toxic response with silver or its salts, in the presence of selenium, Vitamin E and copper should be noted.

Silver has been shown to accentuate copper deficiency in chicken and cattle, presumably by interfering with copper metabolism (Underwood 1979, Smith and Carson 1977).

Silver is also antagonistic to selenium and will reduce the toxic effects associated with elevated levels of selenium in the diet (Jensen et al. 1974). Conversely, silver (100 mg/l in drinking water) promotes liver necrosis characteristic of vitamin E and selenium deficiency in chicks (Ganther et al. 1973). Silver is believed to exert its antagonistic effect on selenium, either through an inhibitory effect on the activity of liver glutathione peroxidase or via decreased biosynthesis of this enzyme due to interference with selenium metabolism (Wagner et al. 1975). Addition of ionic silver to the diet of vitamin-E-deficient rats also causes rapidly fatal hepatocellular necrosis, muscular dystrophy, and brain necrosis (Grasso et al. 1969).

C. SUMMARY

Human exposure to silver can occur through a number of exposure pathways--through ingestion, dermal absorption and inhalation--however all routes are associated with low exposure levels of silver. Typically daily dietary exposure levels range from 35-88 ug; higher levels are likely for certain subpopulations ingesting large quantities of silver-contaminated bran, mushrooms, fish and shellfish. The maximum daily exposure level resulting from ingestion of drinking water is 0.06 mg, which is below the exposure level of 0.1 mg/day which would result from ingestion of water with a silver concentration equivalent to EPA's Drinking Water Standard of 0.05 mg/l.

Exposure to higher levels can be found in subpopulations drinking untreated surface water with concentrations exceeding 10 mg/l (approximately 11% of the samples in STORET). This subpopulation, however, is expected to be extremely small.

The route of dermal absorption appears to be significant only for subpopulations using medicinal products containing silver primarily during treatment of burns. Exposure levels associated with dermal application may be as high as 100 mg per application although not all of this amount would be absorbed. Other potentially significant exposure routes are home developing of photographic film and use of silver solders; however, these do not appear to be associated with a high level of silver uptake.

Inhalation of silver will expose large subpopulations in urban areas to exposure levels of approximately 45 to 185 ng per day; although certain cities have significantly lower air-borne silver levels.

Very small subpopulations may be exposed to significantly higher exposure levels in the vicinity of smelters (approximately 450 mg/day but as high as 1576 mg), steel mills (up to 216 ng/day) and government mints (0.86 mg/day as a worst case, more likely 0.29 mg/day).

In conclusion, the highest exposure levels are associated with very localized atmospheric concentrations of silver affecting a very small subpopulation and with medicinal use of silver-containing products. A small fraction of the U.S. surface water supply, if consumed untreated, would exceed the drinking water criterion. Typical concentrations in drinking water are much lower than the Public Health Service Standard and EPA Water Quality Criterion for human health.

The ingestion of silver, even in trace quantities, has no known beneficial effects as a micronutrient. System human toxicity, however, is rare due to the poor absorption of silver by all routes of exposure (e.g., < 10% by the oral route). The only known consequence of chronic human exposure to silver is argyria, which does not involve significant physiological effects. Argyria is believe to occur at a total body burden of approximately 1g Ag and above.

The possibility of silver acting as a carcinogen in mammals due to ingestion or inhalation has not been studied directly. However, long-term toxicity tests examining other adverse effects in laboratory animals exposed through ingestion have found no increased incidences of tumors. Long-term human occupational exposures, which involve all three routes, have not been linked to carcinogenic effects. Solid silver implants and suspensions of colloidal silver have resulted in tumors in laboratory animals at the site of implantation, but these are considered examples of silver acting as a nonspecific irritant rather than as a specific carcinogen and, therefore, are not of particular relevance to human risk from ingestion of silver. Conflicting mutagenicity data require additional studies for clarification of the mutagenicity of silver. In addition, little is known about the effects of silver on reproduction and/or embryonic development.

In animals, the primary toxic effects of silver are associated with the cardiovascular, hepatic and hematopoietic systems. A broad spectrum of shorter-than-lifetime studies suggest 0.2 mg Ag/1 to be a no-effect concentration of silver in drinking water of laboratory animals. In that this concentration is several fold higher than the maximum reported silver concentration in surface waters of the United States, there appears to be little or no likelihood of acute human poisoning with silver from the environment.

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CHAPTER VII.

RISK CONSIDERATIONS

A. RISK STATEMENT

There is some potential for occurrence of adverse effects in aquatic organisms in certain areas of the U.S. due to exposure to silver. Typical total silver concentrations in surface water sometimes exceed non-lethal effects concentrations (based on laboratory bioassays on ionized silver). An important factor in determining whether potentially toxic levels will cause harm at a specific location is the set of environmental variables at the site. Since, at this time, these factors must be considered on a site-specific basis, the actual environmental significance of silver on a national scale cannot be ascertained.

Silver does not appear to be interfering with microbial processes, in the environment or in wastewater treatment with any great frequency.

Adverse effects are not likely among humans because the silver concentrations in drinking water, food, and air are low relative to the concentrations required to cause effects--sublethal as well as lethal--in humans and laboratory animals. In addition, the rates of absorption by the gastrointestinal tract, skin, and lungs are low, as is the rate of accumulation in tissue.

Discussion of the assumptions and supporting evidence for these conclusions is presented in this chapter.

B. BIOTIC RISK CONSIDERATIONS

Risks to non-human biota are discussed separately for (1) aquatic life in natural waters, excluding microorganisms, (2) microorganisms in natural waters and wastewater treatment systems, and (3) food crops and fish consumable by humans.

1. Aquatic Life in Natural Waters

The risk to aquatic biota of exposure to silver varies considerably by location. Few industry categories regularly practice direct aquatic discharge of high levels of silver because of the economic incentives to recover silver. Approximately 10% of all environmental releases from human activities are made directly to surface water. Inadvertent discharges due to leakage, spills and overflows of holding reservoirs appear more likely to be responsible for any adverse effects in water; however, no specific information is available concerning such discharges.

The impact of any silver release on a local aquatic population depends upon the preexisting background concentrations of silver; the dilution volume and flow rate of the receiving waters, the presence of complexing agents, the pH and hardness of the water, species present, and other factors. In natural waters, silver is found in free ionic form, as soluble AgHS (in the presence of H_2S and HS^-) and in other slightly soluble silver sulfate complexes. A fraction of the total concentration may be in colloidal form or associated with other suspended material such as organic matter, metal hydroxides and iron manganese oxides. The silver held in this reservoir may reenter the water column under certain conditions, such as in the presence of ammonia (Smith and Carson 1977). However, under typical conditions, most of the silver present remains in insoluble form. The equilibrium between dissolved and solid phases of silver is dependent upon pH, the presence of complexing agents, and the redox potential, as described in Section IV.B.

Silver is toxic at low concentrations when its ionic form is available to biota. Therefore, the form of silver to which organisms are exposed is very influential in determining the threshold concentration for effects. The compound, Ag_2S, for example, is relatively insoluble with a low potential for dissociation and, therefore, is not very biologically active. In almost all toxicity studies, silver is used in the form of $AgNO_3$ (Section V.B), which is presumably the most available form due to its complete ionization at test concentrations.

Comparison of effects levels with reported concentrations of silver in the environment is impeded by several factors. For toxicity studies concentrations are reported assuming nearly 100% ionization. Monitoring data, on the other hand, reflect concentrations of total silver, summing levels of all forms of silver, including the ion, complexes, the absorbed fraction in fine suspended material, and so forth.

The percentage available to biota cannot be generalized since the chemical constitution of the water sample in each monitoring observation is required to determine the ionic concentration. Jenne et al. (1978) have published a detailed model predicting the inorganic speciation of silver in natural waters over a range of salinity. Due to the large effort required to estimate silver availability in natural waters in a representative number of locations, such an analysis has not been undertaken for this risk assessment.

From the results of laboratory studies concerning the toxicity of silver to aquatic organisms, general ranges of concentrations can be distinguished and associated with types of effects and species groups (see Table 52). These ranges are by no means strictly defined and exceptions due to species differences or environmental parameters do exist. As mentioned previously, most of the test solutions were prepared using $AgNO_3$ as the source of silver.

TABLE 52. GENERAL RANGES OF SILVER CONCENTRATIONS RESULTING IN EFFECTS ON AQUATIC BIOTA

Concentration	Effect
<0.1 ug/l	No effects reported for any species
0.1-1.0 ug/l	Chronic effects on most sensitive freshwater fish (mortality of trout in soft water) and invertebrates (mayfly LC$_{50}$). Acute effects on most sensitive marine invertebrates. (Sea urchin egg development.)
1.2 ug/l[1]	EPA criterion to protect freshwater aquatic life at water hardness of 50 mg/l as CaCO$_3$.
2.3 ug/l[1] (maximum at any time)	EPA criterion to protect saltwater aquatic life from acute toxicity.
1-10 ug/l	Acute effects on most sensitive freshwater vertebrates (guppy) and invertebrates (daphnia). The typical concentration range for chronic effects on freshwater vertebrates and invertebrates. Chronic effects on most sensitive and typical marine invertebrates.
13 ug/l[1]	EPA criterion to protect freshwater aquatic life at water hardness of 200 mg/l as CaCO$_3$.
10-100 ug/l	Most reported effects levels for freshwater vertebrates and invertebrates fell within this range. Chronic effects (growth retardation) on freshwater algae. Typical range for acute effects on marine invertebrates.
100-1000 ug/l	Includes the highest concentration reported to cause acute and chronic effects on marine invertebrates. (Shrimp LC$_{50}$ at 262 ug/l and no spawning at 103 ug/l). Sublethal effects noted for marine algae in 4 days.
>1000 ug/l	Includes the maximum reported concentration causing acute effects on freshwater invertebrates. (1400 ug/l) reported for rotifer LC$_{50}$) and chronic effects on algae (freshwater) (toxic at 2000 ug/l).

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[1] U.S. EPA (1980).

Source: Chapter V, except as noted.

In considering the concentration ranges causing deleterious effects to aquatic biota reported in Chapter V, several points can be made about the potential exposure of aquatic organisms:

- Concentrations of total silver in surface water, while usually less than 10 ug/l, frequently exceed or overlap the lowest observed range in effects levels for aquatic organisms (see Figure 17) at various locations in the U.S.

- Surface water concentrations are fairly uniformly distributed nationally, with slightly higher than average levels appearing consistently in the Southeast, Ohio River, Lake Erie and Western Gulf major river basins.

- The only river basins that have exhibited increases in mean concentrations recently are the North Atlantic, Southeast and Lower Mississippi while most of the other basins have experienced decreases.

- Although only water hardness has been tested for its influence on silver toxicity, based on observations on metals in general, other environmental variables commonly encountered in natural systems are expected to mitigate the toxic effects of measured total silver concentrations, so that they are not equivalent to concentrations of the highly available compounds used in bioassays.

- Examples of environmental conditions conducive to greater biological availability of silver in surface water[1] include (1) high pH (> 7.0) where desorption and adsorption processes approach the same rate (Klein 1978): (2) presence of ammonia which resolubilizes silver held in suspended sediment (Smith and Carson 1977); (3) high saline levels typical of marine waters, where the concentration of Ag ion is greatly exceeded by that of $AgCl_2^-$, whereas in fresh water Ag^+ and $AgCl_2^-$ concentrations are roughly equivalent although at lower levels than AgHS (Jenne et al. 1978).

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[1] These examples are meant to be illustrative of specific conditions and do not account for other variables that may interfere with these patterns. The set of examples presented is not inclusive of all conditions favorable to ion availability.

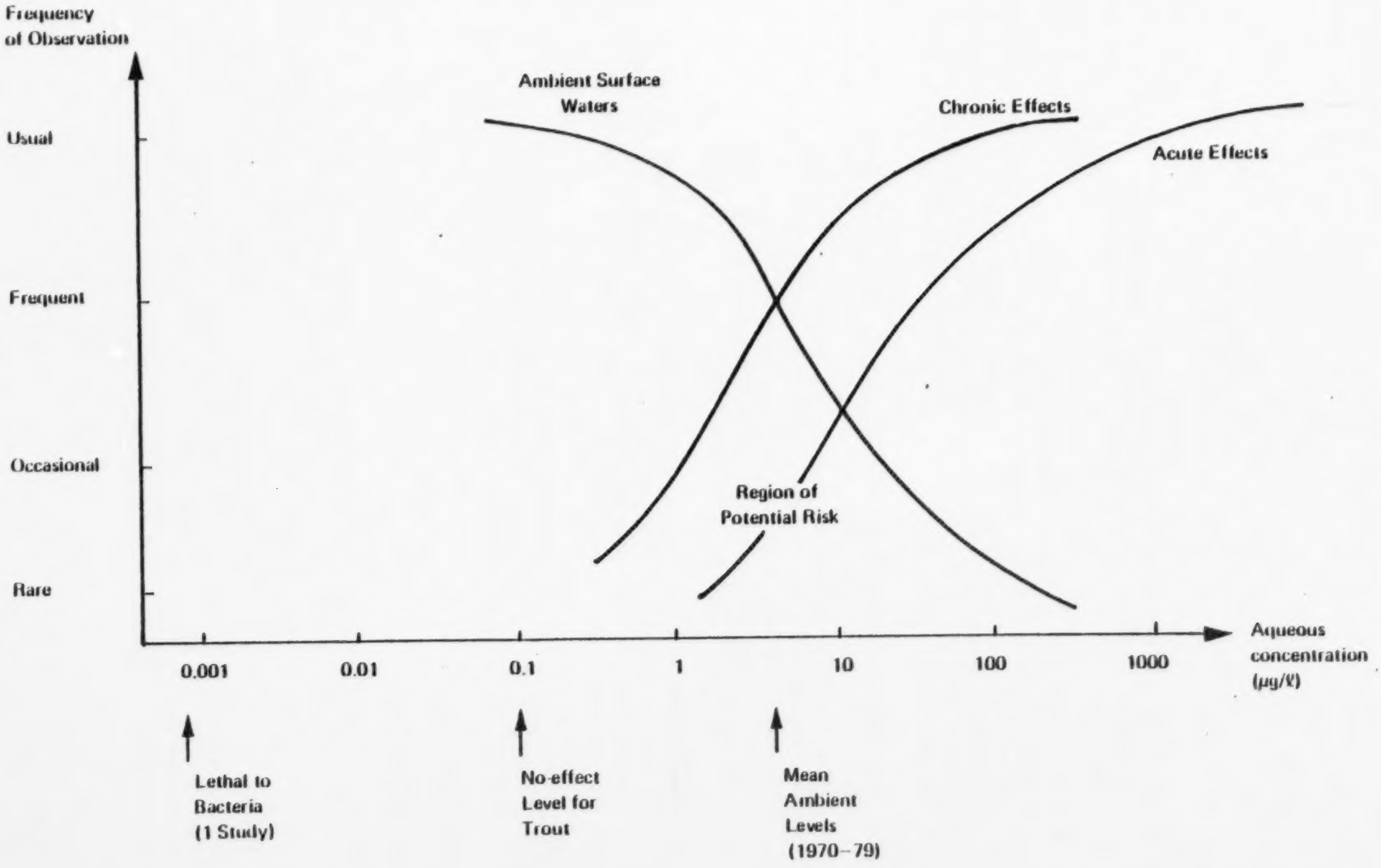

FIGURE 17. SUMMARY OF SILVER EXPOSURE AND EFFECTS FOR FRESHWATER ORGANISMS

- Natural mineral sources of silver are responsible for a large fraction of the silver present in surface water.

- Materials balance data (Chapter III) indicate that the photography industry is the primary direct discharger of silver to surface water, releasing approximately 119 kkg annually (207 kkg including discharges to POTWs) largely in the form of insoluble sulfides and thiosulfate complexes.

- The majority of environmental releases of silver (77%) are to land and are in a relatively inert, solid form (e.g., metal wastes, conductors). Fate data (Chapter IV) do not indicate substantial transfer of silver from soil to water through leaching due to its strong adsorptability, although runoff of contaminated surface soil may be significant at some locations.

- Only 6% of all environmental releases are to air and only 2 kkg of silver is used annually in cloud-seeding activities. Hence, silver contributions from the atmosphere to water are expected to be small.

- Much of the silver released in the past deposits in in sediments as silver sulfide, while a small fraction cycles in the environment.

2. Microorganisms

a. Cloud Seeding

There has been concern that environmental discharge of silver, particularly in the form of AgI nucleating agents, may interfere with microbial processes in soil, water and wastewater treatment. However, there is no evidence that the 2 kkg of silver used annually in weather modification activities has any adverse impact on microbial populations on a large scale (see Chapter V-A). The only exception may be in the immediate vicinity of cloud-seeding generators, where a slight decrease in the decay of organic matter has been observed. The total area in the United States expected to be affected in this way is small.

b. Sludge

The disposal of industrial and municipal sludge onto land (approximately 220 kkg annually) may also result in the adverse exposure of soil microbial populations. Sludge levels range from 100 mg/kg up to 900 mg/kg. When the sludge is mixed with the soil, the sludge levels would be decreased even further. This does not mean to imply, however, that microbial processes are unaffected by sludge-derived levels; effects will be dependent upon the environmental characteristics of the treated site.

Lower effects levels for microbial processes in soil, on the order of 60 mg/kg, have been reported in laboratory studies. The 15% of municipal sludge used for amending agricultural soil may interfere with processes essential to the cycling of nitrogen, sulfur and organic matter. No toxicity or exposure data directly relating to the species responsible for these processes were available to indicate threshold effects concentrations. In addition no data were available reporting soil levels of silver resulting from sludge application.

Other non-waste disposal related, soil concentrations (see Section IV.E) are usually reported to be significantly lower than the effects levels cited earlier, averaging 0.37 mg/kg in industrial areas and 0.19 mg/kg in agricultural areas.

Silver appears to be quite immobile in soil (Section IV.C). It is likely to accumulate in the vicinity of a continual release and to remain in the surface layer. The problem of availability appears again in interpreting the potential bioaccumulation and toxicity of soil concentrations to terrestrial organisms. A large fraction of the total amount detected is unavailable for plant uptake due to complexation and adsorbtion by organic matter, clay and oxides. A smaller fraction may be in the form of insoluble silver sulfide in anaerobic soils (Smith and Carson 1977).

c. Wastewater Treatment

There has been speculation that silver may interfere with microbial processes in wastewater treatment due to its microbiocidal effects at low concentrations. Typical ambient concentrations of silver in surface waters are usually lower than those triggering effects in sewage treatment plants (10-25 mg/kg as reported in Section IV.B).

Although effects concentrations as low as 0.001 ug/l have been determined in laboratory studies, much lower than typical silver concentrations in wastewater influent (usually ~50 ug/l - Section IV.B), it is unlikely that the influent levels have the same effects on sewage treatment microbial populations as those observed in the laboratory.

Much of the silver entering a treatment facility, 50-70%, is removed by sedimentation before reaching the activated sludge process (Smith and Carson 1977). Therefore, both reduction in silver concentrations in the waste stream due to nonbiological processes prior to reaching the microbial populations and the partial biological availability of the silver present help to reduce the potential for toxic effects of silver during wastewater treatment.

3. Biota of Significance to Human Exposure

Ingestion of silver-contaminated food is a significant route of human exposure as discussed in Section VI.A. Because bioaccumulation of high silver levels by biota will occur in areas where significant exposure to silver is occurring, bioaccumulation in species consumed by humans is briefly reconsidered here.

Theoretically significant bioaccumulation of silver may occur in food crops grown on sludge-amended soil. Although no studies directly addressing this subject were available--silver is generally not included in metal uptake studies--some general conclusions can be drawn from other studies on terrestrial plants. Silver appears to accumulate in the root zone in elemental form, with some translocation to other plant compartments. Concentrations of approximately 20 mg/kg and higher have been reported for plants exposed to AgI or $AgNO_3$ in soil.

The only concentrations of silver in soil treated with wastewater effluents reported were 1.0 mg/kg-2.4 mg/kg (Olson et al. undated) (see Section 3.C.3). Smith and Carson (1977) reported concentrations in sludge of up to 900 mg/kg which could contribute high silver levels to amended soil. These concentrations are much higher than those employed in laboratory studies and could support at least minimal silver bioaccumulation in food crops assuming environmental conditions conducive to uptake and accumulation in the edible fraction of the plant.

Studies on bioaccumulation of other metals such as Cd, Cu and Zn from sludge reveal plant concentrations are commonly two to three orders of magnitude above soil concentrations (Perwak et al., 1980a,b,c). However, the limited data on silver indicate plant tissue levels no greater than 2 to 3 times the soil level (see Section IV.D). Silver is relatively nontoxic to humans compared with certain other metals usually present in sludge (mercury, lead) and thus, relatively, does not appear to be a significant problem in terms of crop uptake from sludge-amended soil.

A number of species of aquatic organisms commonly ingested by humans accumulate high tissue levels of silver. The fish tissue levels (total body) reported in the STORET data base (see Section IV.D) typically ranged from 20 mg/kg wet weight to a maximum of 1,900 mg/kg; the mean level over the years sampled, 1975-1979, was 235 mg/kg (221 observations). Bioconcentration factors[3] calculated on a dry weight basis range from 2 to 10 for total body and up to 330 for specific organs, based on limited data for two species of fish. In invertebrates such as the red abalone and the rock scallop, concentrations equivalent to those measured in fish are reported (Section IV.D). Tissue levels higher than control levels (three to ten times) have been related to certain silver sources: sewage outfalls, industrial areas, waste disposal sites, and electroplating facilities.

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[3] Concentration in tissue divided by concentration in water.

The implications of accumulated silver in biota to human exposure and risk are discussed in the following section.

C. HUMAN RISK CONSIDERATIONS

The most significant human exposure, in terms of amount, to silver is its medicinal use in topical preparations. However, the duration of this form of exposure and the size of the exposed subpopulation is small. In addition, the relative benefits of using these compounds may make them the preferred treatment. Almost all other individual exposure routes occur at levels at least three orders of magnitude lower compared to long-term daily medicinal exposure levels of 50 mg/day which may occur during treatment of severe, widespread burns.

Table 53 summarizes exposure level ranges derived previously in Section VI.A. Only inhalation exposure in the vicinity of a government mint (∿10 mg/day) approached that of medicinal application; however, the degree of absorption may not be equivalent for these two routes. Inhalation in the vicinity of other silver sources was associated with very low exposures, on the order of 10-500 ng/day.

In Table 54 three exposure scenarios are presented in order to estimate the magnitude of maximum levels of silver to which humans are likely to be exposed. One scenario results in a maximum exposure of 0.13 mg/day for a large fraction of the U.S. population, and is attributable to ingestion of food and treated drinking water for the most part. Also included is the amount of silver added by exposure to urban air, in the absence of a specific source, which is nearly identical to that for rural populations near a smelter or mining operation (less than 0.001 mg/day difference). A second scenario combines ingestion of contaminated food, unfinished drinking water and inhalation near a source. This results in an exposure of 1.35 mg/day. The size of this subpopulation (ingesting unfinished drinking water with high silver concentration) is expected to be quite small. Thus the likelihood of this exposure level being achieved is remote.

TABLE 53. ESTIMATED EXPOSURE LEVELS OF SILVER FOR HUMANS

Exposure Pathway	Silver Range of Exposure Levels	Estimated Size of Subpopulation Exposed
Medicinal Applications	∼50 mg in one application	Very Small
Developing Film	Usually low; see VI.A.3.b.	Very Small
Ingestion of Food[1]	18 - 103 ug/day	220.6 X 10^6 (general population)[2]
Ingestion of Drinking Water		
• Unfinished drinking water	0.1 - 790 ug/day	Very Small
• Tap water	26 - 30 ug/day	Large (50% of U.S. population)
• Well water	0 - 30 ug/day	Large (50% of U.S. population)
Inhalation of Silver in Air		
• Urban areas	47 - 186 ng/day	165.5 X 10^6[3]
• Non-Urban areas	6 - 7 ng/day	55 X 10^6[3]
• In vicinity of sources	200 - 450 ng/day	Small
• In vicinity of mint	9,860,000 ng/day	Extremely Small

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[1] Based on three estimations of dietary intake (see VI,A.2).

[2] U.S. Department of Commerce (1980).

[3] Based on an extrapolation of 1970 data on urban and rural population distribution to 1980 census data.

Source: Chapter VI

TABLE 54. SILVER EXPOSURE SCENARIOS FOR HUMANS EXPOSED TO MULTIPLE SOURCES

Exposure Scenario	Exposure Level[1]	Estimated Size of Subpopulation
Ingestion of food, ingestion of tap or drinking water, inhalation of urban background or in vicinity of rural source such as a smelter or mining operation.	0.13 mg/day	Large
Ingestion of food, ingestion of unfinished drinking water, inhalation as noted above.	1.35 mg/day	Small
Use of silver ointment, ingestion of food, ingestion of unfinished drinking water and inhalation as noted above.	58 mg/day	Very Small

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[1] From upper limit data presented in Table 53.

The third exposure scenario (58 mg/day), although exceeding the extrapolated effects level, is even more unlikely to occur than the second one because it assumes both medicinal use during burn treatment and ingestion of unfinished drinking water. The chances for this combination of circumstances are believed to be very slim.

Table 55 summarizes the effects levels for mammals discussed in Chapter V. The lowest reported lethal dose is very high--10 g orally for silver nitrate--but this level cannot be directly compared with effects concentrations for silver ion alone because the toxicity of silver nitrate is partially attributed to its caustic properties. No lethal level was available for the ion itself. The threshold for the sublethal effect, mild argyria, could be approached after around 55-60 years, at an intake rate of 58 ug daily.

Comparison of effects and exposure levels reveals that none of the individual exposure pathways described in Tables 53 and 54 or any reasonable combination of them will result in serious human effects for the majority of the U.S. population. Figure 18 shows the relationship between individual exposure levels and effects levels for the routes of inhalation and ingestion. The most likely potential effect, based on exposure levels, would be mild argyria. If one assumes a 50% absorption efficiency (experimental evidence suggests 10%) across the gut and 55 years of exposure, the lowest exposure level to result in argyria would be less than one order of magnitude greater than levels commonly found in drinking water. However, lowering the absorption efficiency estimate to 25% means that over 100 years of exposure would be required to produce argyria.

In conclusion, the risk to humans of adverse effects resulting from exposure to silver is believed to be quite low.

TABLE 55. ADVERSE EFFECTS OF SILVER ON MAMMALS

Adverse Effect	Species	Lowest Reported Effect Level	No Detected Effect Level
Argyria	man	not well defined ∿1g Ag tissue accumulation	<1g Ag tissue accumulation
Carcinogenesis			
• oral	---[1]	no data	---
• implantation	rat	solid implants induce tumors only at site of implantation	300-mesh Ag 75 mg/rat
Mutagenesis			
• bacteria	*Bacillus subtilis*	---	0.72% AgCl
• mammalian cells	hamster	enhanced cell transformation 0.001% $AgNO_3$	---
Vascular hypertension	rat	635 mg Ag/L drinking water, 30 months	
Right ventricular hypertrophy			
Kidney hemorrhaging	rat	0.4 mg Ag/l drinking water - duration not given[2]	0.2 mg Ag/l drinking water 6 mo.
Reduced conditioned reflex activity	rat	0.5 mg Ag/l drinking water - 11 months	0.2 mg Ag/L drinking water 6 months
Acute lethality	mouse	LD_{50} 100 mg colloidal Ag/kg - orally	---
By ingestion	man	Minimum Lethal Dose 10 g $AgNO_3$	---

[1] Dashes mean unknown.

[2] Equivalent to exposure level for 70 kg-human of 28 mg/day, assuming a 2-month exposure period.

Source: Chapter VI.

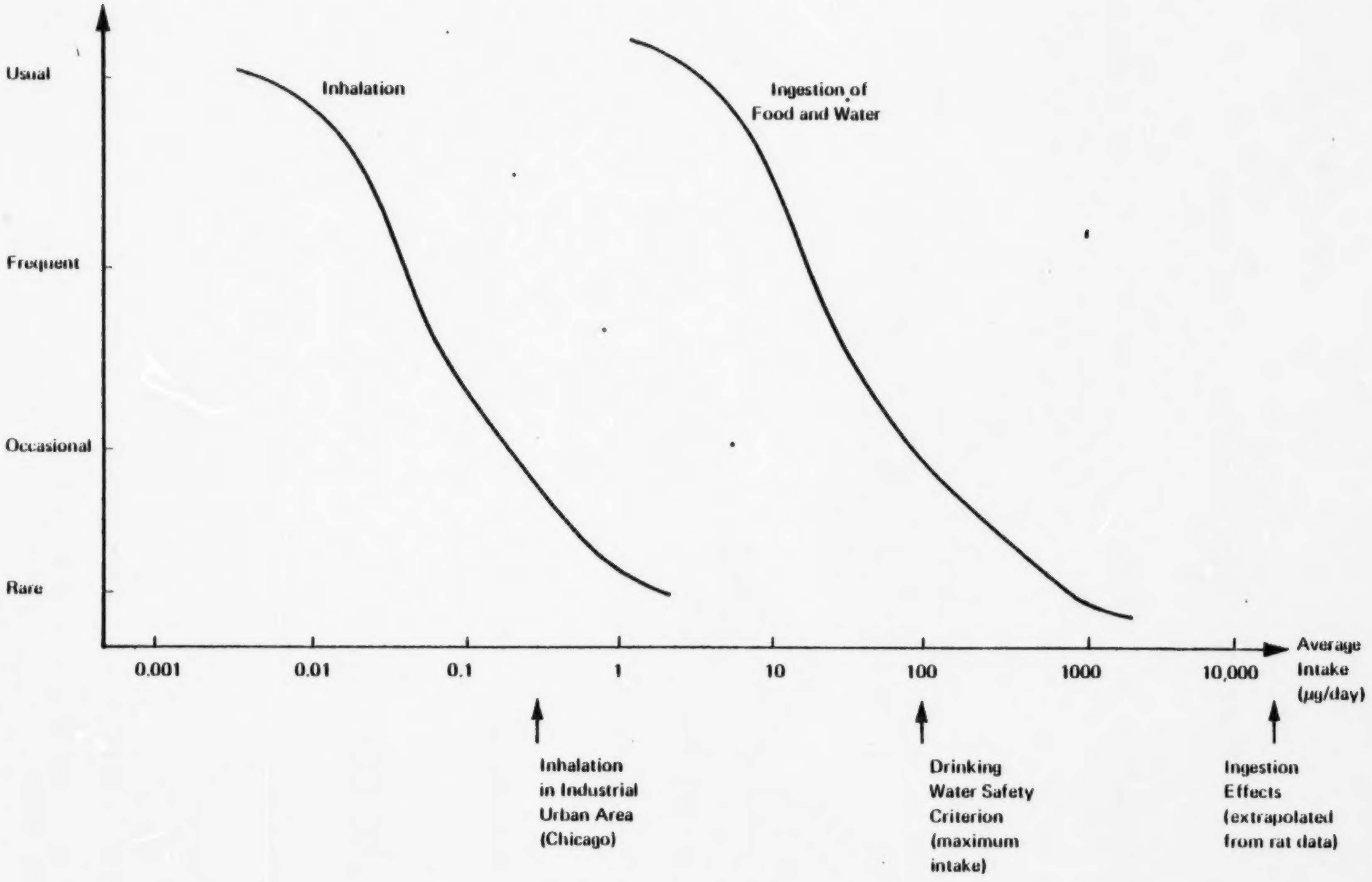

FIGURE 18. SUMMARY OF CHRONIC HUMAN EXPOSURE DUE TO INGESTION OR INHALATION OF SILVER

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APPENDIX A. PRELIMINARY DATA FOR SILVER CONSUMPTION - 1979

End Use	Consumption (kkg)
Photography	2050
Electrical/Electronic Products	
Contacts/Conductors	1040
Batteries	140
Sterling Ware	410
Brazing Alloys/Solders	340
Catalysts	240
Electroplated Ware	250
Jewelry	170
Coins, Medallions & Commemorative Objects	90
Dental/Medical	70
Mirrors	60
Bearings	10
Coinage	5
Miscellaneous	30
TOTAL	4905

Source: Drake (1980).

APPENDIX B. MAPS SHOWING RATIO OF Ag CONCENTRATION IN WHOLE WATER TO CRITERIA AGGREGATED BY COUNTY

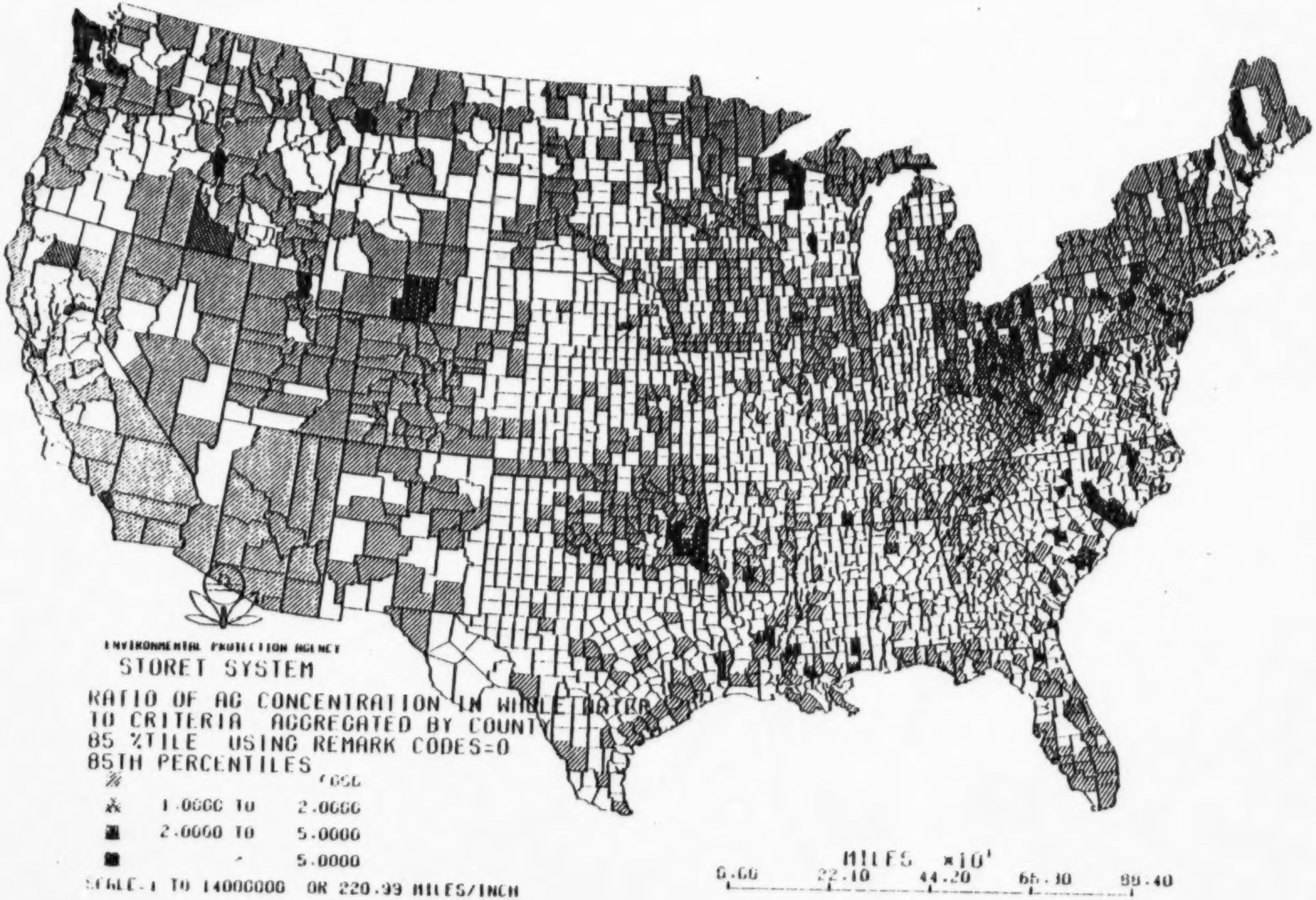
ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
RATIO OF AG CONCENTRATION IN WHOLE WATER
TO CRITERIA AGGREGATED BY COUNTY
85 %TILE USING REMARK CODES=0
85TH PERCENTILES
1.0000 TO 2.0000
2.0000 TO 5.0000
5.0000
SCALE-1 TO 14000000 OR 220.99 MILES/INCH
MILES ×10¹
0.00
22.10
44.20
66.30
88.40

FIGURE B-1. RATIO OF AG CONCENTRATION IN WHOLE WATER TO CRITERIA AGGREGATED BY COUNTY 85 %TILE USING REMARK CODES=0 85TH PERCENTILES

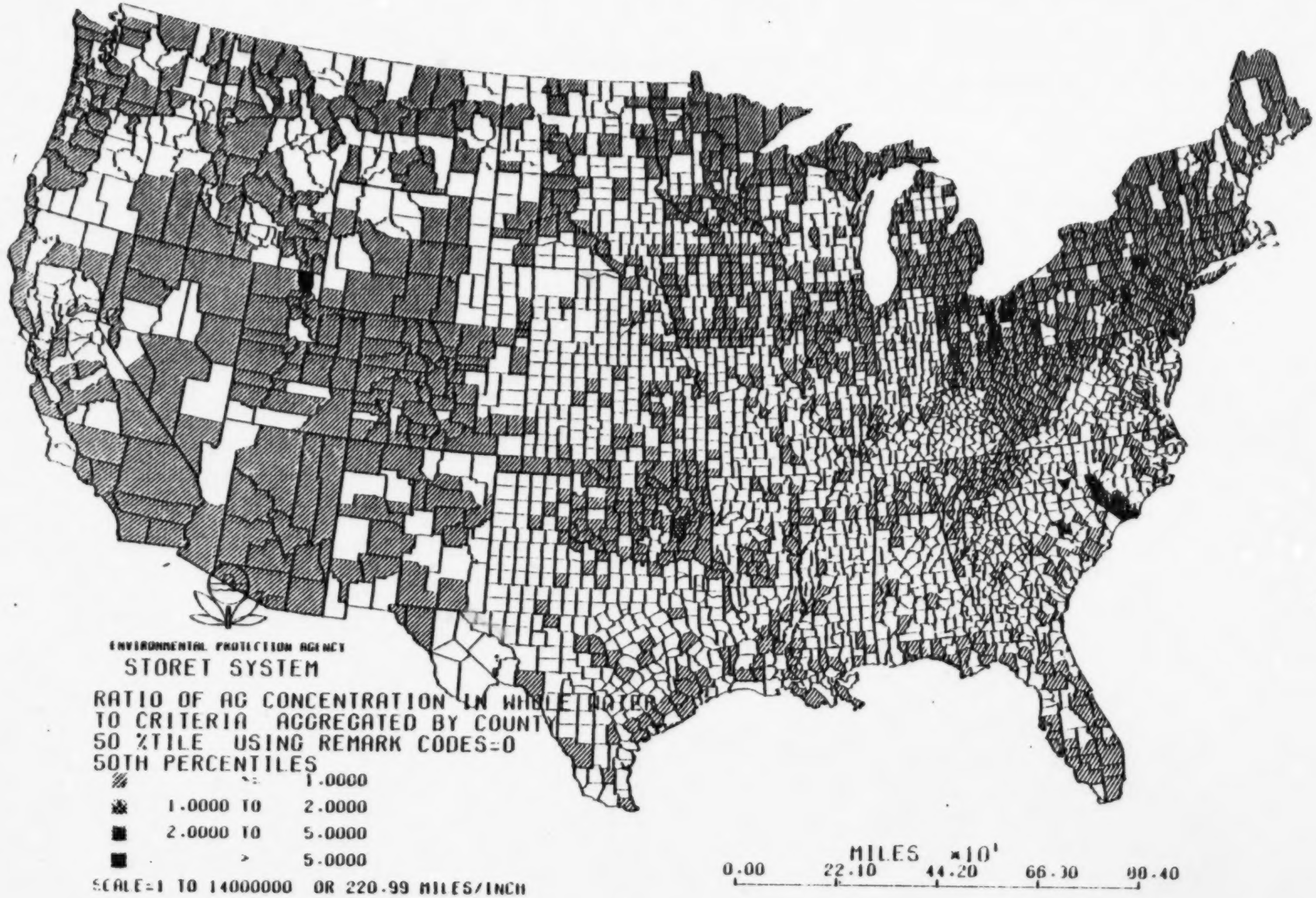
ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
RATIO OF AG CONCENTRATION IN WHOLE WATER
TO CRITERIA AGGREGATED BY COUNTY
50 %TILE USING REMARK CODES=0
50TH PERCENTILES
<= 1.0000
1.0000 TO 2.0000
2.0000 TO 5.0000
> 5.0000
SCALE=1 TO 14000000 OR 220.99 MILES/INCH
MILES ×10¹
0.00
22.10
44.20
66.30
88.40

FIGURE B-2. RATIO OF AG CONCENTRATION IN WHOLE WATER TO CRITERIA AGGREGATED BY COUNTY 50 %TILE USING REMARK CODES=0 50TH PERCENTILES

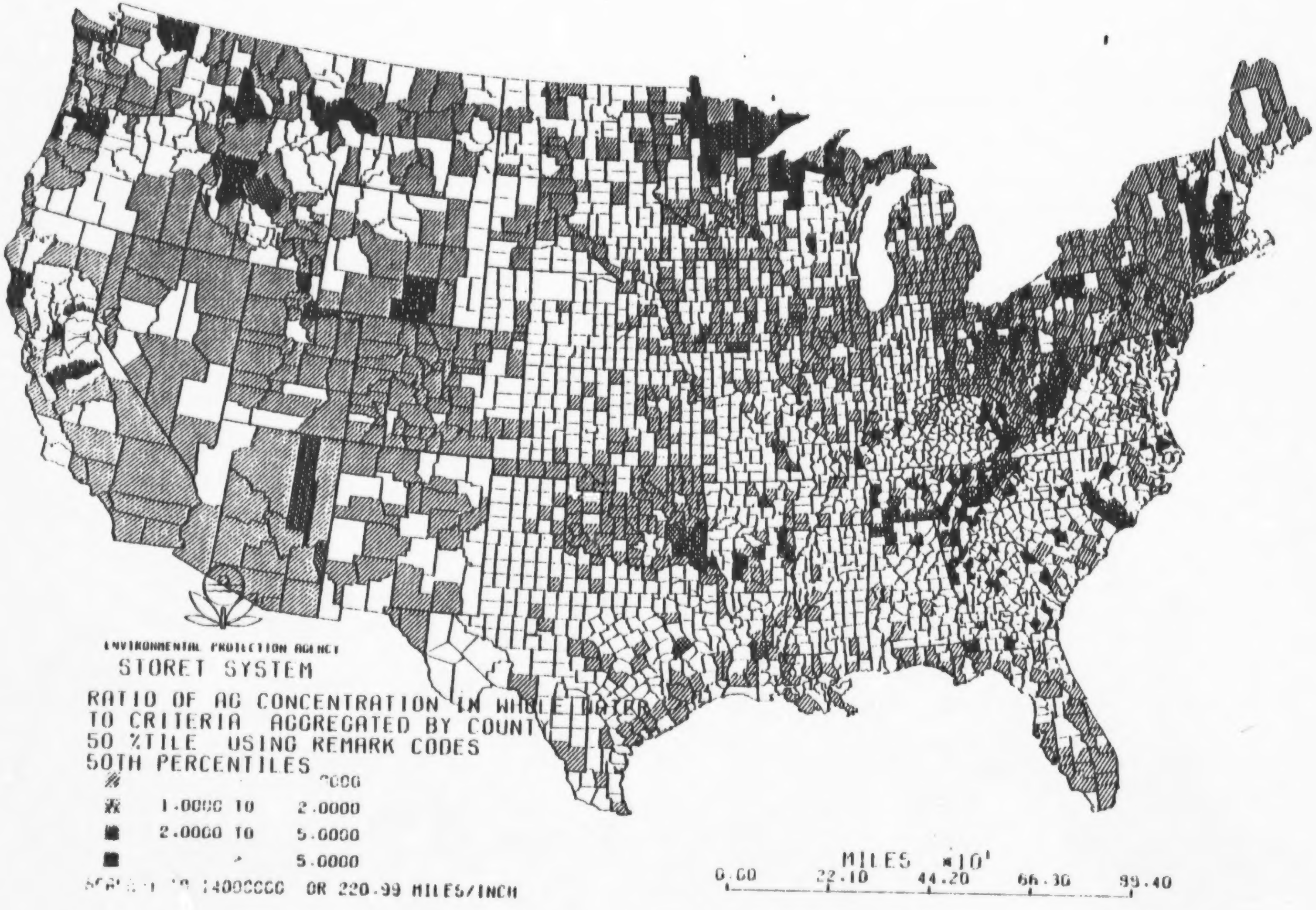
ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
RATIO OF AG CONCENTRATION IN WHOLE WATER
TO CRITERIA AGGREGATED BY COUNTY
50 %TILE USING REMARK CODES
50TH PERCENTILES
.0000
1.0000 TO 2.0000
2.0000 TO 5.0000
> 5.0000
14000000 OR 220.99 MILES/INCH
MILES *10¹
0.00
22.10
44.20
66.30
88.40

FIGURE B-3. RATIO OF AG CONCENTRATION IN WHOLE WATER TO CRITERIA AGGREGATED BY COUNTY 50 %TILE USING REMARK CODES 50TH PERCENTILES